GEORGIA INSTITUTE OF TECHNOLOGY
OFFICE OF CONTRACT ADMINISTRATION
SPONSORED PROJECT INITIATION

Date: 2/12/81

oject Title: A Kinetics Investigation of Several Key Tropospheric Chemical Reactions

oject No: A-2856

oject Director s: Dr. A. R. Ravishankara and Dr. P. H. Wine

onsor: National Science Foundation; Washington, D. C. 20550

reement Period: From 12/15/80 Until 5/31/83
(Includes usual 6 month unfunded flexibility period)

pe Agreement: Grant No. ATM-8019040

nount: $122,766 NSF
6,461 GIT (E-242-416)
$129,227 TOTAL

ports Required: Annual Progress Report; Final Project Report

onsor Contact Person (s):

Technical Matters

chard A. Carrigan
F Program Officer
mospheric Chemistry Program
vision of Atmospheric Sciences
rectorate for Astronomical, Atmospheric,
Earth, and Ocean Sciences
tional Science Foundation
shington, D. C. 20550
2/357-9657

Contractual Matters
(thru OCA)

Mary Frances O'Connell
NSF Grants Official
Section II
AAEO/EAS Branch
Division of Grants and Contracts
Directorate for Administration
National Science Foundation
Washington, D. C. 20550
202/357-9602

ense Priority Rating: None

igned to: EML/SSD (School/Laboratory)

IES TO:

roject DirectorS
ivision Chief (EES)
chool/Laboratory Director
ean/Director—EES
ccounting Office
rocurement Office
ecurity Coordinator (OCA)
~~eports Coordinator (OCA)~~

Library, Technical Reports Section
EES Information Office
EES Reports & Procedures
Project File (OCA)
Project Code (GTRI)
Other

3 (3/76)

GEORGIA INSTITUTE OF TECHNOLOGY OFFICE OF CONTRACT ADMINISTRATION

SPONSORED PROJECT TERMINATION SHEET

Date 4/14/83

Project Title: A Kinetics Investigation of Several Key Tropospheric Chemical Reactions

Project No: A-2856

Project Director: A. R. Ravishankara & Paul H. Wine

Sponsor: National Science Foundation

Effective Termination Date: 5/31/83

Clearance of Accounting Charges: 5/31/83

Grant/Contract Closeout Actions Remaining:

- [ ] Final Invoice and Closing Documents
- [x] Final ~~Fiscal~~ Acctg. Report (FCTR)
- [x] Final Report of Inventions
- [x] Govt. Property Inventory & Related Certificate
- [ ] Classified Material Certificate
- [ ] Other _____

Assigned to: EML (~~School~~/Laboratory)

COPIES TO:

Administrative Coordinator	Research Security Services	EES Public Relations (2)
Research Property Management	Reports Coordinator (OCA)	Computer Input
Accounting	Legal Services (OCA)	Project File
Procurement/EES Supply Services	Library	Other/ Wine

FORM OCA 10:781

A-2856

A KINETICS INVESTIGATION OF SEVERAL KEY TROPOSPHERIC CHEMICAL REACTIONS

An Interim Progress Report on

Grant No. ATM-80-19040

Submitted to:

National Science Foundation
Directorate for Astronomical, Atmospheric, Earth, and Ocean Sciences
Division of Atmospheric Sciences
Washington, D.C. 20550

For the Time Period:

December 15, 1980 - December 15, 1981

By

Molecular Sciences Branch
Physical Sciences Division
Electromagnetics Laboratory
Engineering Experiment Station
Georgia Institute of Technology
Atlanta, Ga. 30332

Co-Principal Investigators:

Dr. A.R. Ravishankara Dr. P.H. Wine

PROGRESS DURING THE PERIOD 12/15/80 - 12/15/81

During the first year of our current NSF grant, we focused our attention primarily on tropospheric sulfur chemistry. Three separate studies are described below:

(1) The flash photolysis-resonance fluorescence technique was employed to study the kinetics of OH radical reactions with $H_2S(k_1)$, $CH_3SH(k_2)$, $CH_3SCH_3(k_3)$, and $CH_3SSCH_3(k_4)$ over the temperature range 244-367 °K. The following Arrhenius expressions adequately describe the measured rate constants as a function of temperature (units are cm^3-$molecule^{-1}s^{-1}$): $k_1 = (6.4 \pm 1.3) \times 10^{-12} \exp[-55 \pm 58)/T]$; $k_2 = (1.15 \pm 0.39) \times 10^{-11} \exp[(+338 \pm 100)/T]$; $k_3 = (6.8 \pm 1.1) \times 10^{-12} \exp[(-138 \pm 46)/T]$; $k_4 = (5.9 \pm 3.3) \times 10^{-11} \exp[(+380 \pm 160)/T]$. A manuscript which describes this work, compares the results with previous investigations, and discusses the atmospheric implications of the results was recently published in the Journal of Physical Chemistry; a copy is attached as Appendix A.

(2) Electronically excited $CS_2(CS_2^*)$ was found to be rapidly produced in the troposphere by absorption of solar photons (lifetime of CS_2 toward conversion to CS_2^* is a few hours). It was shown that the reaction of CS_2^* with O_2 can remove tropospheric CS_2 on a time scale of one or two weeks if the CS + SOO yield from this reaction is greater than 0.01. Assuming a ground level background CS_2 concentration of 20 pptv and a COS lifetime of 1 year, our calculations indicate that the photooxidation mechanism can be a major source of tropospheric COS but only a minor source of SO_2. A manuscript describing this work was published recently in Geophysical Research Letters; a copy is attached as Appendix B.

(3) The reactions of OH radicals with $CH_3SH(k_2)$ and $CS_2(k_5)$ were re-investigated over a much broader range of experimental conditions than were employed in our previous investigations. k_2 was found to be independent of pressure in the presence of chemically inert buffer gases and also independent of $[O_2]$ at O_2 partial pressures up to a few Torr. Hence, the fast rate constant measured by Cox and Sheppard (Nature 284, 330 (1980)] (a factor of three faster than obtained in our study or a similar study by Atkinson, et al. [J. Chem. Phys. 66, 1578 (1977)]) cannot be attributed to differences in the pressure regimes of the studies. k_5 was found to increase significantly when a few Torr of O_2 were added to the reaction mixture. The large differences in rate constants reported by Cox and Sheppard (Nature 284, 330 (1980)] vs. Wine, et al. [J. Phys. Chem. 85, 2499 (1980)] and Iyer and Rowland (Geophys. Res. Lett. 7, 797 (1980)] appear to be attributable to the dependence of k_5 on $[O_2]$. A manuscript describing the above experiments will be published soon in the Proceedings of the Second Symposium on the Composition of the Nonurban Troposphere (sponsored by NASA). This manuscript also describes some initial results of an ongoing study of the reaction $OH + SO_2 + M \longrightarrow HSO_3 + M$. A copy of the manuscript is attached as Appendix C.

FUTURE EXPERIMENTS

During the remainder of the grant period we expect to complete our study of the pressure and temperature dependence of the rate constant for the reaction

$$OH + SO_2 + M \longrightarrow HSO_3 + M,\ M = Ar,\ N_2,\ SF_6$$

and extend our studies of the dependence of k_2 and k_5 on $[O_2]$ to higher oxygen concentrations. To obtain the required detection sensitivity, an apparatus featuring pulsed laser induced fluorescence detection of OH is being constructed. We also expect to initiate, and in come cases complete, studies of the following important tropospheric reactions:

$$OH + CH_3OOH \longrightarrow CH_3O_2 + H_2O$$

$$I(^2P_{3/2}) + O_3 \longrightarrow IO + O_2$$

$$I(^2P_{3/2}) + HO_2 \longrightarrow HI + O_2$$

$$OH + HI \longrightarrow I(^2P_J) + H_2O\ .$$

In our original proposal, studies of methoxy radical reactions were included. However, a recent study by Gutman, et al. (J. Phys. Chem. 82, 66 (1982)], demonstrated that $CH_3O + O_2$ is the only important methoxy radical reaction under atmospheric conditions. The direct measurement of Gutman, et al. gave a rate constant which agreed well with previous indirect studies. Hence, we no longer feel that CH_3O chemistry is a high research priority.

APPENDIX A

Reprint of

"Kinetics of OH Reactions with Atmospheric Sulfur Compounds H_2S, CH_3SH, CH_3SCH_3, and CH_3SSCH_3"

Kinetics of OH Reactions with the Atmospheric Sulfur Compounds H_2S, CH_3SH, CH_3SCH_3, and CH_3SSCH_3

P. H. Wine,* N. M. Kreutter, C. A. Gump, and A. R. Ravishankara*

Molecular Sciences Group, Engineering Experiment Station, Georgia Institute of Technology, Atlanta, Georgia 30332
(Received: April 10, 1981; In Final Form: June 1, 1981)

The flash photolysis–resonance fluorescence technique has been employed to study the kinetics of hydroxyl radical reactions with H_2S (k_1), CH_3SH (k_2), CH_3SCH_3 (k_3), and CH_3SSCH_3 (k_4) over the temperature range 244–367 K. The following Arrhenius expressions adequately describe the measured rate constants as a function of temperature (units are cm^3 $molecule^{-1}$ s^{-1}): $k_1 = (6.4 \pm 1.3) \times 10^{-12} \exp[(-55 \pm 58)/T]$; $k_2 = (1.15 \pm 0.39) \times 10^{-11} \exp[(+338 \pm 100)/T]$; $k_3 = (6.8 \pm 1.1) \times 10^{-12} \exp[(-138 \pm 46)/T]$; $k_4 = (5.9 \pm 3.3) \times 10^{-11} \exp[(+380 \pm 160)/T]$. The results are compared with previous investigations, and their implications regarding reaction mechanisms and atmospheric sulfur chemistry are discussed.

Introduction

The atmospheric sulfur cycle has been the subject of intensive investigation in recent years because of the need to assess the contribution of anthropogenically produced sulfur to acid rain, visibility reduction, and climate modification. In heavily industrialized regions such as the eastern United States and western Europe, anthropogenic sulfur emissions exceed natural emissions by 1 order of magnitude.[1] On a global scale, however, natural sulfur emissions are thought to approximately equal those from anthropogenic sources.[2,3] Prediction of adverse effects which may result from anthropogenic sulfur emissions thus requires an understanding of the natural sulfur cycle.

Biological reduction of sulfur compounds is generally believed to be a major natural source of atmospheric sulfur.[2-4] A number of reduced sulfur compounds have been detected in the atmosphere including COS (carbonyl sulfide), CS_2 (carbon disulfide), H_2S (hydrogen sulfide), CH_3SH (methyl mercaptan), CH_3SCH_3 (dimethyl sulfide), and CH_3SSCH_3 (dimethyl disulfide).[5]

With the probable exception of COS and CS_2, atmospheric degradation of reduced sulfur compounds is believed to be initiated by reaction with OH radicals:

$$OH + H_2S \xrightarrow{k_1} SH + H_2O \quad (1)$$

$$OH + CH_3SH \xrightarrow{k_2} \text{products} \quad (2)$$

$$OH + CH_3SCH_3 \xrightarrow{k_3} \text{products} \quad (3)$$

$$OH + CH_3SSCH_3 \xrightarrow{k_4} \text{products} \quad (4)$$

The initial step in understanding the atmospheric chemistry of reduced sulfur species is to accurately establish the rates of reactions 1–4 over the tropospheric temperature range. $k_1(T)$–$k_4(T)$ can be used in conjunction with measured and/or calculated OH concentrations to obtain atmospheric residence times. Where concentration data are available (i.e., H_2S and CH_3SCH_3) source strengths can be computed from known residence times and loss rates.

Some kinetic data are reported in the literature for each of the reactions 1–4, with reaction 1 being the most studied and reaction 4 the least studied. Direct measurements of k_1 have been reported by several investigators using both flash photolysis[6-8] and discharge flow[9,10] techniques. k_1(298 K) values range from 3.1×10^{-12} to 5.5×10^{-12} cm^3 $molecule^{-1}$ s^{-1} while the reported activation energies range from 0 to 880 kcal/mol. Leu and Smith[10] report a non-Arrhenius temperature dependence with $k_1(T)$ going through a minimum in the range 265–300 K. The data of Michael et al.[8] support this unusual temperature dependence although these authors point out that a temperature-independent k_1 would also be consistent with their data. The only direct measurement of k_2, a flash photolysis–resonance fluorescence study by Atkinson et al.,[11] reports $k_2 = 8.9 \times 10^{-12} \exp(+400/T)$ cm^3 $molecule^{-1}$ s^{-1} for $299 < T < 426$ K. There have been two flash photolysis–resonance fluorescence studies of reaction 3 which are in excellent agreement,[12,13] the combined results giving $k_3 = 6.1 \times 10^{-12} \exp(+134/T)$ for $273 < T < 426$ K. No direct measurements of k_4 have been reported. In addition to the above results, indirect determinations of rate constants for reactions 1–4 at 297 K have been reported by Cox and Sheppard.[14] These investigators measured k_1–k_4 relative to the rate constant for the reaction of OH with ethylene (assumed to be 8.0×10^{-12} cm^3 $molecule^{-1}$ s^{-1}) and obtained $k_1 = 5.0 \times 10^{-12}$, $k_2 = 9.0 \times 10^{-11}$, $k_3 = 9.1 \times 10^{-12}$, and $k_4 = 2.2 \times 10^{-10}$ cm^3 $molecule^{-1}$ s^{-1}. It is clear that only in the case of k_3 is there good agreement of several independent studies. Furthermore, very few data exist at temperatures relevant for atmospheric modeling (i.e., $T < 298$ K).

In this paper we report the results of a flash photolysis–resonance fluorescence kinetics study of reactions 1–4 over the temperature range 244–367 K. The data are compared with previously reported results, and their mechanistic and atmospheric implications are discussed.

(1) J. N. Galloway and D. M. Whelpdale, *Atmos. Environ.*, 14, 409 (1980).
(2) C. F. Cullis and M. M. Hirschler, *Atmos. Environ.*, 14, 1263 (1980).
(3) L. Granat, H. Rodhe, and R. O. Hallberg, in "Nitrogen, Phosphorous, and Sulphur—Global Cycles", B. M. Svensson and R. Söderlund, Eds., SCOPE Report 7, Swedish Natural Science Research Council, Stockholm, 1976, pp 89–134.
(4) H. Rodhe and I. Isaksen, *J. Geophys. Res.*, 85, 7401 (1980).
(5) T. E. Graedel, *Rev. Geophys. Space Phys.*, 15, 421 (1977).
(6) F. Stuhl, *Ber. Bunsenges. Phys. Chem.*, 78, 231 (1974).
(7) R. A. Perry, R. Atkinson, and J. N. Pitts, Jr., *J. Chem. Phys.*, 64, 3237 (1976).
(8) J. V. Michael, D. F. Nava, W. D. Brobst, R. P. Borkowski, and L. J. Stief, *J. Phys. Chem.*, submitted.
(9) A. A. Westenberg and N. deHaas, *J. Chem. Phys.*, 59, 6885 (1973).
(10) M. T. Leu and R. H. Smith, *J. Phys. Chem.*, submitted.
(11) R. Atkinson, R. A. Perry, and J. N. Pitts, Jr., *J. Chem. Phys.*, 66, 1578 (1977).
(12) R. Atkinson, R. A. Perry, and J. N. Pitts, Jr., *Chem. Phys. Lett.*, 54, 14 (1978).
(13) M. J. Kurylo, *Chem. Phys. Lett.*, 58, 233 (1978).
(14) R. A. Cox and D. Sheppard, *Nature (London)*, 284, 330 (1980).

I: Monitoring Wavelengths and Absorption Cross Employed to Measure the Fraction of Reactant eactant/Ar Storage Bulbs

eactant	monitoring wavelength, nm	absorption cross section, 10^{-19} cm^2
S	185.0 (Hg lamp)	38.2
H_3SH	228.8 (Cd lamp)	6.70
H_3SCH_3	228.8 (Cd lamp)	11.6
H_3SSCH_3	185.0 (Hg lamp)	159

nental Section

pparatus used in this study has been described ly.[15] Hence, only a brief review of its operation below.

eted Pyrex reaction cell with an internal volume cm^3 was used in all experiments. The cell was ed at a known constant temperature by circulating ene glycol–water mixture from a thermostated ough the outer jacket. OH radicals were produced photolysis of H_2O at wavelengths between the absorption at 185 nm and the Suprasil cutoff at n. An OH resonance lamp situated perpendicular ash lamp excited fluorescence in the 0–0 band of $^+$–$X^2\pi$ system. Fluorescence was detected per- ar to both the flash lamp and the resonance lamp otomultiplier fitted with an interference filter peak transmission, 100-Å fwhm). Signals were d by photon counting and then fed into a signal operating in the multichannel scaling mode. For ay rate measured, sufficient flashes were averaged a well-defined temporal profile over at least two ally three $1/e$ times. The flash duration was ~50 measured OH lifetimes ranged from 0.95 to 43 ms. er to avoid accumulation of reaction or photolysis s, all experiments were carried out under "slow nditions. Reactant (i.e., H_2S, CH_3SH, CH_3SCH_3, SCH_3) was flowed from a 12-L bulb containing a eactant/Ar mixture. An H_2O/Ar mixture was d by bubbling Ar through high-purity water at nperature and a pressure of 800 torr. The reactant the H_2O mixture, and additional diluent gas were d before entering the reaction cell. Concentrations component in the reaction mixture were deter- rom measurements of the appropriate mass flow d the total pressure.

raction of reactant in the reactant/Ar mixture was frequently by simultaneous measurement of the ssure (of the mixture) and UV absorption by the . Atomic line sources were used in conjunction 82-cm absorption cell and a band-pass filter– ltiplier detector to carry out these measurements. nitoring wavelength and the absorption cross mployed to measure each reactant are summarized I. The needed absorption cross sections were d during the course of the investigation and found well with published values[16] in all cases.

ases used in this study had the following stated Ar ≥ 99.9995%, H_2S ≥ 99.5%, and CH_3SH ≥ H_2S and CH_3SH were degassed repeatedly at 77 e use. Ar was used as supplied. CH_3SCH_3 and CH_3 were obtained in liquid form from Eastman Chemicals; sample purities are typically in the –99%.[17] The liquid samples were transferred into Pyrex tubes fitted with high-vacuum stopcocks, degassed several times at 77 K, and then stored under vacuum on a gas handling system. The tube containing CH_3SSCH_3 was blackened to prevent absorption of room light. The samples were subjected to additional degassing immediately before use. UV spectra of vapor-phase samples of CH_3SH, CH_3SCH_3, and CH_3SSCH_3 were run on a Cary 17 spectrophotometer. The spectra agreed very well in both wavelength dependence and absorption coefficient with published spectra;[16] 100 torr of CH_3SCH_3 sample gave no measurable absorption at 280 nm, indicating less than 0.1% CH_3SSCH_3 contamination.

Results

To measure the desired bimolecular rate constants, it is desirable to establish experimental conditions where the OH temporal profile is governed by the following processes:

$$H_2O \xrightarrow{h\nu} H + OH \quad (5)$$

$$OH + R_i \xrightarrow{k_i} \text{products} \qquad i = 1\text{–}4,\ R_i = \text{reactant} \quad (6)$$

$$OH \xrightarrow{k_d} \text{loss by diffusion from field of view of detector and reaction with background impurities} \quad (7)$$

Then, if [R] ≫ [OH] (pseudo-first-order conditions), simple first-order kinetics will be obeyed:

$$\ln \{[OH]_0/[OH]_t\} = (k_i[R] + k_d)t \equiv k't \quad (I)$$

The bimolecular rate constant, k_i, is determined from the slope of a k' vs. [R] plot. Observation of OH temporal profiles which are exponential (i.e., obey eq I), a linear dependence of k' on [R], and invariance of k_i to variations in experimental parameters such as the flash intensity and the water concentration serve as proof that reactions 5–7 are, indeed, the only processes which affect the OH time history and, therefore, validate the measurement of k_i. (The presence of reactive impurities in the reactant sample will, of course, not be detected by such a kinetic analysis.)

Under typical operating conditions (flash energy ≈ 60 J, $[H_2O]$ = 0.15 torr) 5×10^{10}–10×10^{10} OH radicals cm^{-3} are produced by the photoflash.[15] Therefore, we did not expect reactions of OH with itself or with reaction products to contribute to the observed temporal profile. This expectation was confirmed experimentally by showing that k_i was not affected by a factor of 3 reduction in $[H_2O]$ at constant flash intensity.

To investigate the possibility that reactive free radicals generated by photodissociation of reactants could contribute to the observed OH temporal behavior, we carried out experiments where the flash intensity was varied by a factor of 3 or more at constant $[H_2O]$. Only in the case of reaction 1 was evidence observed for secondary chemistry complications. Measurements at flash energies of ~120 J gave k_1 values which were 10–15% higher than those measured at lower flash energies. No dependence of k_1 on flash energy was observed in the 20–72-J range, so the high flash intensity data were ignored in the determination of k_1.

Because reaction 4 was found to proceed at a near gas kinetic rate, CH_3SSCH_3 concentrations as low as 1×10^{12} molecules cm^{-3} were used in some experiments. To ensure the existence of pseudo-first-order conditions, therefore, all measurements of k_4 employed $[H_2O]$ = 0.06 torr. Under these experimental conditions, all OH decays were found to be exponential for more than two $1/e$ times (Figure 1).

H. Wine, N. M. Kreutter, and A. R. Ravishankara, *J. Phys.* , 3191 (1979), and references therein.
G. Calvert and J. N. Pitts, Jr., "Photochemistry", Wiley, New 6.

(17) R. Hawryluk, Eastman Organic Chemicals, private communication.

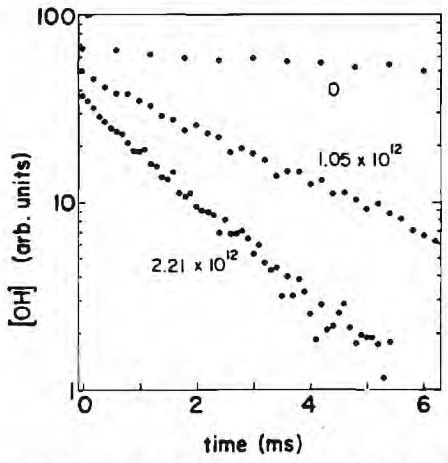


Figure 1. Typical OH temporal profiles observed following flash photolysis of H_2O/Ar/reactant mixtures. Reactant: CH_3SSCH_3. Experimental conditions: $T = 249$ K; $P = 50$ torr; $P_{H_2O} = 0.06$ torr; flash energy = 61 J; CH_3SSCH_3 concentrations in units of molecules cm^{-3} are given in the figure.

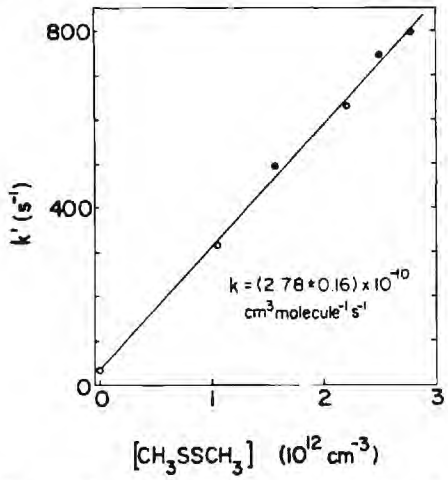


Figure 2. Typical k' vs. [R] data. Reactant: CH_3SSCH_3. Experimental conditions: $T = 249$ K; $P = 50$ torr; $P_{H_2O} = 0.06$ torr; flash energy = 61 J. The open circles represent the three pseudo-first-order rate constants determined from the data shown in Figure 1. The line is obtained from an unweighted linear least-squares analysis.

Furthermore, k_4 was found to be independent of a factor of 3 (39–115 J) variation in flash energy. Hence, we are confident that none of the results for reaction 4 requires correction for deviation from first-order kinetics.

A total of 319 experiments (experiment ≡ determination of one pseudo-first-order rate constant) were carried out. For each reaction studied varying conditions of pressure, temperature, water concentration, and flash intensity were employed. Typical OH temporal profiles are shown in Figure 1. A typical plot of k' vs. [R] is shown in Figure 2. Exponential OH decays and linear dependences of k' on [R] were observed in all cases. None of the rate constants was found to be pressure dependent over the ranges investigated (40–120 torr of Ar for H_2S and CH_3SH, 50–200 torr of Ar for CH_3SCH_3 and CH_3SSCH_3). The experimental results are summarized in Table II. Errors quoted for individual k_i determinations are 2σ and refer only to the precision of the k' vs. [R] data. Where two or more k_i's were averaged to obtain a rate constant, the overall precision is conservatively chosen to bracket all individual k_i's and their 2σ uncertainties. In the three cases where only one $k_i(T)$ was determined, the uncertainty is set at ±15%, which is a little larger than the typical uncertainty observed when several determinations were averaged. The

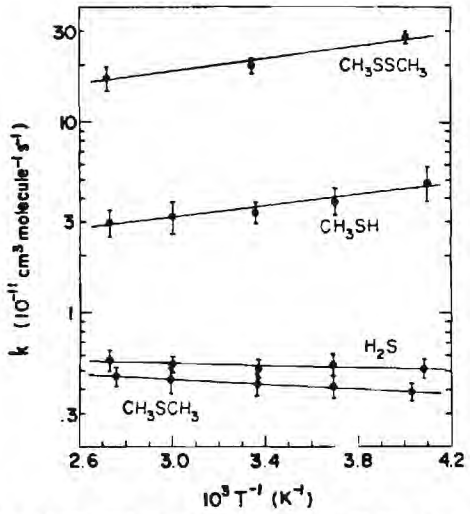


Figure 3. Arrhenius plots of the experimental results. Errors are chosen so as to bracket all measured $k_i \pm 2\sigma$ values.

absolute accuracy of the results is limited by both precision and uncertainties in the determination of the reactant concentration. We estimate the absolute accuracy of $k_i(T)$ to be better than 20%.

The data for each of the four reactions investigated are adequately described in Arrhenius form (i.e., a linear ln k vs. T^{-1} dependence). Unweighted linear least-squares analyses give the following Arrhenius expressions (units are cm^3 $molecule^{-1}$ s^{-1}):

$$k_1 = (6.4 \pm 1.3) \times 10^{-12} \exp[(-55 \pm 58)/T]$$

$$k_2 = (1.15 \pm 0.39) \times 10^{-11} \exp[(+338 \pm 100)T]$$

$$k_3 = (6.8 \pm 1.1) \times 10^{-12} \exp[(-138 \pm 46)/T]$$

$$k_4 = (5.9 \pm 3.3) \times 10^{-11} \exp[(+380 \pm 160)T]$$

The errors in the above expressions are 2σ and represent precision only. The experimental rate constants and best-fit Arrhenius lines are plotted in Figure 3. The temperature dependence observed for k_1 was so weak that a temperature-independent rate constant of $(5.35 \pm 0.40) \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1} would also be an adequate representation of the data.

Discussion

Kinetic data obtained in this investigation are compared with results from other laboratories in Figures 4 and 5.

With the exception of the discharge flow–ESR study of Westenberg and deHaas,[9] there is general agreement that reaction 1 has little or no temperature dependence over the range of temperatures relevant to the atmosphere. In a discharge flow–resonance fluorescence study Leu and Smith[10] observed an unusual temperature dependence with $k_1(T)$ actually going through a minimum when $T \approx 280$ K. Michael et al.,[8] using the flash photolysis–resonance fluorescence technique, report rate constants at three temperatures (228, 298, and 437 K) which support the findings of Leu and Smith. However, these authors point out that a temperature-independent k_1 would also be an adequate representation of their data. Our results and those of Perry et al. are not sufficiently precise and do not cover a broad enough temperature range to either support of refute the temperature dependence observed by Leu and Smith. It is interesting to note that the results of all temperature-dependent studies "converge" in the tropospheric temperature regime such that, for $230 < T < 300$ K, a value $k_1 = (4.6 \pm 1.0) \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1} is

E II: Rate-Constant Data for the Reactions of OH with H_2S, CH_3SH, CH_3SCH_3, and CH_3SSCH_3

reaction	T, K	P, torr	P_{H_2O}, torr	flash energy, J	linear flow rate,[a] cm s^{-1}	no. of experiments	$10^{12}(k_i \pm 2\sigma)$, cm^3 molecule^{-1} s^{-1}	av $10^{12}k_i$,[b] cm^3 molecule^{-1} s^{-1}
OH + H_2S	245	40	0.12	20	2.1	8	5.18 ± 0.58	
		40	0.12	120	2.1	6	5.97 ± 0.43[c]	
		40	0.10	39	2.1	5	5.14 ± 0.23	5.16 ± 0.56
	271	95	0.19	61	2.0	5	5.22 ± 0.17	
		40	0.15	72	2.1	7	5.49 ± 0.57	
		40	0.15	31	2.1	5	5.46 ± 0.25	5.39 ± 0.67
	297	44	0.19	61	2.3	6	5.06 ± 0.30	
		40	0.05	61	2.1	6	5.33 ± 0.26	
		40	0.15	31	2.1	8	5.10 ± 0.36	
		40	0.15	39	2.1	7	5.03 ± 0.47	5.13 ± 0.57
	333	40	0.16	61	2.2	5	5.53 ± 0.36	
		40	0.15	31	2.1	8	5.30 ± 0.26	5.41 ± 0.48
	366	40	0.15	115	2.1	7	6.24 ± 0.73[c]	
		40	0.15	39	2.1	7	5.76 ± 0.58	
		120	0.14	72	3.1	4	5.51 ± 0.45	
		120	0.15	72	1.0	6	5.76 ± 0.40	
		40	0.15	20	2.1	7	5.63 ± 0.56	5.66 ± 0.68
OH + CH_3SH	244	40	0.13	65	2.1	6	53.7 ± 4.4	
		40	0.15	65	2.1	6	49.2 ± 1.8	
		120	0.14	65	1.0	5	49.5 ± 1.6	
		120	0.13	65	3.1	5	40.9 ± 1.6	48.3 ± 9.8
	270	40	0.15	72	2.1	9	38.4 ± 2.4	38.4 ± 5.8
	298	40	0.15	39	2.1	5	33.8 ± 3.0	
		40	0.15	115	2.1	6	34.8 ± 1.8	
		40	0.05	72	2.1	4	32.4 ± 2.8	
		40	0.13	65	2.1	6	33.9 ± 1.5	33.7 ± 4.1
	333	40	0.15	72	2.1	7	29.7 ± 1.6	
		40	0.15	72	2.1	5	34.6 ± 3.8	32.2 ± 6.2
	366	40	0.15	39	2.1	5	29.5 ± 4.5	
		40	0.14	65	2.1	6	28.4 ± 0.9	
		40	0.15	115	2.1	6	32.3 ± 1.7	
		120	0.15	72	1.0	7	29.2 ± 3.6	
		120	0.15	72	3.0	6	29.2 ± 1.0	29.7 ± 4.7
OH + CH_3SCH_3	248	50	0.11	31	1.6	6	3.99 ± 0.23	
		50	0.13	125	1.4	4	3.78 ± 0.29	3.89 ± 0.38
	271	50	0.12	31	1.6	5	4.31 ± 0.12	
		50	0.13	125	1.6	6	4.33 ± 0.37	
		100	0.11	72	1.5	6	3.82 ± 0.15	4.15 ± 0.55
	298	50	0.15	72	1.5	6	4.37 ± 0.44	
		50	0.14	72	1.5	7	4.14 ± 0.24	
		50	0.05	72	1.6	6	4.23 ± 0.53	
		50	0.15	20	1.5	6	4.21 ± 0.30	
		50	0.15	72	1.6	4	4.33 ± 0.43	4.26 ± 0.56
	334	50	0.15	31, 125	1.5	7	4.50 ± 0.30	4.50 ± 0.68
	363	50	0.14	72	1.6	5	4.50 ± 0.34	
		200	0.15	72	1.5	5	4.80 ± 0.19	
		100	0.13	72	1.6	6	4.70 ± 0.38	4.67 ± 0.51
OH + CH_3SSCH_3	249	50	0.06	61	3.0	5	282 ± 15	
		50	0.06	61	3.0	6	278 ± 16	280 ± 18
	298	50	0.06	39	3.0	4	192 ± 10	
		50	0.06	115	3.0	3	203 ± 7	
		200	0.06	61	2.9	4	191 ± 11	
		50	0.06	61	3.0	4	204 ± 3	198 ± 18
	367	50	0.06	61	3.0	5	171 ± 10	171 ± 25

ar flow rate ≡ measured mass flow rate (units of standard cm^3 s^{-1}) × 760/P(torr) divided by the cross-sectional area eactor. [b] Uncertainties are chosen to bracket all measured rate constants including their 2σ errors. Where only a was determined, the uncertainty is assumed to be ±15% in keeping with the uncertainties observed in the other [c] Due to suspected secondary chemistry complications, these data were not included in the determination of the av-lue of $k_i(T)$.

nt with all available data except the 298 K result .[6] Thus, it appears that k_1 is known with reason-uracy for the purpose of atmospheric modeling. r, the unusual temperature dependence observed and Smith suggests that the mechanism may be at more complex than a simple H atom abstraction. tudy of reaction 2 is in excellent agreement with r flash photolysis–resonance fluorescence study son et al.[11] Cox and Sheppard,[14] using competitive kinetics techniques, report a value for k_2 at 298 K about a factor of 3 larger than what is obtained from either direct measurement. These authors suggest that reaction 2 may be faster under their conditions (1 atm of air) than under the reduced pressure conditions employed in the flash photolysis studies. We find k_2 to be independent of pressure over the range 40–120 torr of Ar. This finding does not, however, preclude the possibility of a small termolecular channel which becomes much more important

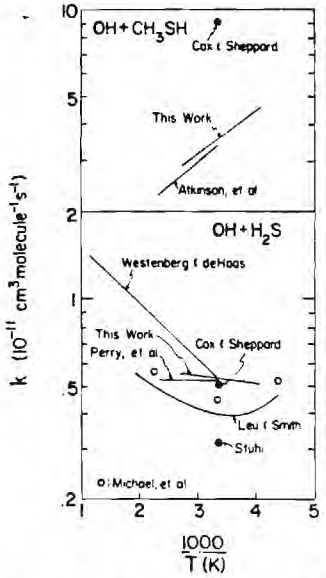


Figure 4. Comparison of our results for reactions of OH with H_2S and CH_3SH with those of other investigators.

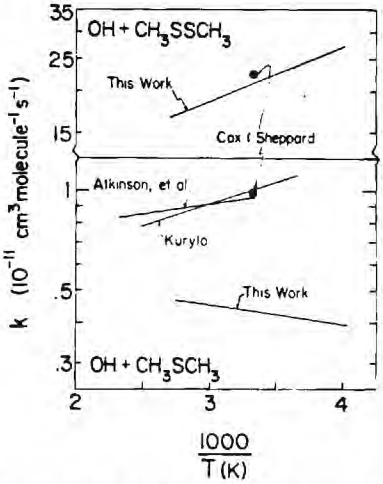


Figure 5. Comparison of our results for the reactions of OH with CH_3SCH_3 and CH_3SSCH_3 with those of other investigators. The line representing Kurylo's data was generated by taking his $k_3(T)$ values and carrying out an unweighted linear least-squares analysis of ln k_3 vs. T^{-1}.

at 1-atm pressure and in the presence of more efficient third bodies. It is also possible that a weakly bound $CH_3SH\cdots OH$ complex, if formed, could react with O_2 before decomposing. A similar mechanism has been proposed to account for the observed pressure-dependent rate constant for the reaction of OH with CO.[18] Clearly, a direct measurement of k_2 under conditions of atmospheric pressure and gas composition would be desirable.

The most interesting result obtained in this investigation is our determination that k_3 is more than a factor of 2 lower than the value obtained (with excellent agreement) in three other laboratories.[12-14] Furthermore, we observe a small positive temperature dependence whereas two previous investigations both report a small negative temperature dependence.[12,13] One major difference between our study and the two previous flash photolysis studies[12,13] is the spectral distribution of the photoflash. We employed Suprasil optics which transmit only at $\lambda > 165$ nm while both earlier studies employed lithium fluoride optics which transmit at $\lambda > 105$ nm. The potential for secondary chemistry involving CH_3SCH_3 photofragments was, therefore, greater in the earlier studies than in our study. Both previous studies, however, report k_3 to be independent of flash intensity, a fact which argues against secondary chemistry involving reactant photofragments being the reason for their higher k_3 values. Another potential explanation for the discrepancies between our results and the two previous flash photolysis studies is the possibility that reactive impurities were present in the CH_3SCH_3 samples used in the earlier investigations. The major impurities in CH_3SCH_3 samples are CH_3SH and CH_3SSCH_3,[17] but, upon exposure to air, CH_3SH is oxidized to CH_3SSCH_3.[19] Our values for k_3 and k_4 predict that reaction of OH with a mixture containing 98% CH_3SCH_3 and 2% CH_3SSCH_3 should give almost exactly the magnitude and temperature dependence reported for k_3 in the two previous flash photolysis studies. It is worth noting, however, that our own experience indicates that handling CH_3SCH_3 is not particularly difficult. The competitive kinetics study of Cox and Sheppard[14] directly monitoried the disappearance of CH_3SCH_3 during continuous OH production by near-UV photolysis of HONO. Hence, this study could not have been affected by either of the potential sources of error discussed above. However, as in any indirect study, interpretation of the results requires a complete understanding of system chemistry. If CH_3SCH_3 was consumed by processes other than reaction 3, overestimation of k_3 would result.

The values for $k_3(T)$ reported in this investigation are very similar in both magnitude and T dependence to those reported for the reaction of OH with CH_3OCH_3 by Perry et al.[20] These authors calculated a rate constant per C–H bond of 5.8×10^{-13} cm^3 molecule^{-1} s^{-1} at 299 K, in excellent agreement with the results of Greiner[21] that, for OH attack on secondary C–H bonds in alkanes (which are similar in strength to the C–H bonds in CH_3OCH_3), the rate constant per bond is $\sim 5.6 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K. From this comparison it was concluded that OH attack on CH_3OCH_3 proceeds with the same mechanism as OH attack on secondary alkanes, namely, H atom abstraction. For CH_3SCH_3, we obtain a rate constant per C–H bond of 7.1×10^{-13} cm^3 molecule^{-1} s^{-1} at 298 K, which strongly suggests that the dominant reaction path is H atom abstraction. The slightly larger rate constant per bond for CH_3SCH_3 vs. CH_3OCH_3 probably reflects a weaker C–H bond in the former although a small but significant addition channel cannot be eliminated as a possibility.

Our results for k_4 are in excellent agreement with the 298 K measurement of Cox and Sheppard. Since reaction 4 is ~ 50 times faster than reaction 3, it must be that OH reaction with CH_3SSCH_3 proceeds primarily by attack at the weak S–S bond. The observed negative temperature dependence provides evidence that an adduct is initially formed, although rapid decomposition to $CH_3S + CH_3SOH$ is quite likely.

Implications for Atmospheric Chemistry

Our results confirm that OH radicals react rapidly with all hydrogen-containing reduced sulfur compounds of atmospheric importance. We can obtain maximum tropospheric residence times, τ_i, from the following relationship:

$$\tau_i^{-1} = k_i[\mathrm{OH}] \qquad \text{(II)}$$

(18) H. W. Biermann, C. Zetsch, and F. Stuhl, *Ber. Bunsenges. Phys. Chem.*, **82**, 633 (1978).

(19) J. D. Roberts and M. C. Caserio, "Basic Principles of Organic Chemistry", W. A. Benjamin, New York, 1965.

(20) R. A. Perry, R. Atkinson, and J. N. Pitts, Jr., *J. Chem. Phys.*, **67**, 611 (1977).

(21) N. R. Greiner, *J. Chem. Phys.*, **53**, 1070 (1970).

re [OH] is an average value over the appropriate time rval. OH levels are highly variable, depending upon local concentrations of O_3, H_2O, CO, CH_4, and NO_x, also the solar UV flux. Recent measurements[22] suggest the annually and diurnally averaged OH concentration he tropical marine boundary layer is 2×10^6 molecules ^{3}. Using this value as a rough estimate for the average H] encountered by reduced sulfur compounds in the er troposphere, we obtain the following lifetimes from results for k_i at 298 K: $\tau_{H_2S} = 27$ h, $\tau_{CH_3SH} = 4.1$ h, $_{SCH_3} = 33$ h, and $\tau_{CH_3SSCH} = 42$ min. Midday OH levels a factor of ~3 larger than the diurnally averaged ues, so the residence times of the short-lived species $_3SH$ and CH_3SSCH_3 will be a factor of 3 shorter at lday than the diurnally averaged estimates suggest. ne current problem in atmospheric sulfur chemistry ters around determining the origin of the relatively high 100 pptv), uniformly distributed SO_2 levels recently asured in the upper troposphere.[23] Because of their rt lifetimes, none of the compounds studied in this estigation can be transported from their ground (or an) sources to the upper troposphere. Therefore, only here exist airborne sources can hydrogen-containing uced sulfur compounds be precursors for free tropos-ric SO_2 (SO_2 itself is removed by OH and heteroge-us processes with a lifetime of ~10 days; hence, the formly distributed SO_2 levels imply the existence of a rly uniformly distributed precursor).

Whereas H_2S is generally thought to enter the atmosphere primarily from localized sources such as swamps and marshes, recent measurements indicate that the ocean is the primary source of CH_3SCH_3 with the diurnally averaged concentration over the ocean being 58 pptv.[24] Model calculations[25] using the combined results of Atkinson et al.[12] and Kurylo[13] for $k_3(T)$, and assuming unit conversion of CH_3SCH_3 to SO_2, demonstrate that oxidation of CH_3SCH_3 can produce ~100 pptv SO_2 in the marine boundary layer—ca. twice the measured concentration.[23] Our values for $k_3(T)$ would reduce the calculated SO_2 source by a factor of ~2.3.

Neither CH_3SH nor CH_3SSCH_3 has been observed in the atmosphere except in the vicinity of large anthropogenic or biogenic sources. However, the very rapid rates at which these species react with OH suggest that undectectably low steady-state concentrations could be present even though reasonably large-scale sources exist. This is particularly true of CH_3SSCH_3. A CH_3SSCH_3 source equal to that for CH_3SCH_3 would imply an atmospheric CH_3SSCH_3 concentration of ~1 pptv, a level which may not be measurable with presently available techniques.

Acknowledgment. We thank D. H. Semmes and R. C. Shah for assisting with some of the experiments and Professor W. L. Chameides for helpful discussions concerning the atmospheric implications of our results. This work was supported by the National Science Foundation through grant no. ATM-80-19040.

22) D. D. Davis, W. L. Chameides, D. Philen, W. Heaps, A. R. Rankara, and M. Rodgers, *J. Geophys. Res.*, submitted.
23) P. J. Maroulis, A. L. Torres, A. B. Goldberg, and A. R. Bandy, *J. phys. Res.*, 85, 7345 (1980).
(24) P. J. Maroulis and A. R. Bandy, *Science*, 196, 647 (1977).
(25) J. A. Logan, M. B. McElroy, S. C. Wofsy, and M. J. Prather, *Nature (London)*, 281, 185 (1979).

APPENDIX B

Reprint of

"Potential Role of CS_2 Photooxidation in Tropospheric Sulfur Chemistry"

GEOPHYSICAL RESEARCH LETTERS, VOL. 8, NO. 5, PAGES 543-546, MAY 1981

POTENTIAL ROLE OF CS_2 PHOTOOXIDATION IN TROPOSPHERIC SULFUR CHEMISTRY

P. H. Wine,[1] W. L. Chameides,[2] and A. R. Ravishankara[a]

Georgia Institute of Technology
Atlanta, GA 30332

Abstract. Electronically excited CS_2 (CS_2*) is found to be rapidly produced in the troposphere from the absorption of solar photons by ground state CS_2 molecules. The chemical reaction of CS_2* with O_2 can, if the CS + SOO yield is greater than 0.01, remove tropospheric CS_2 on a time scale of one or two weeks. Assuming a ground level background CS_2 concentration of 20 pptv and an OCS lifetime of 1 year, calculations indicate that this photooxidation mechanism can be a major source of tropospheric OCS but only a minor source of SO_2.

Introduction

Oxidation of carbon disulfide (CS_2) may lead to the production of carbonyl sulfide (OCS), the predominant sulfur containing compound in the troposphere [Hanst, et al, 1975; Torres, et al, 1980]. OCS is relatively inert in the troposphere and hence can be transported to the stratosphere where it photodissociates rapidly. Oxidation of the resulting sulfur atoms is believed to contribute significantly to the formation of stratospheric sulphate aerosol [Crutzen, 1976], thus affecting the earth's radiation budget and climate. For this reason, there is considerable current interest in identifying the sources of atmospheric OCS.

The potential importance of CS_2 oxidation as a source for OCS (and also SO_2) has been discussed in several recent papers [Sze and Ko, 1979 a, b; Logan, et al, 1979; Turco, et al, 1980]. In all cases, however, the oxidation mechanism was assumed to be initiated by hydroxyl radical attack on CS_2:

$$OH + CS_2 \longrightarrow SH + OCS \qquad (1)$$

$k_1 = 1.9 \times 10^{-13}$ cm^{3}molecule^{-1}s^{-1} [Kurylo, 1978].

Furthermore, background CS_2 levels of $\geq$ 70 pptv [Sandalls and Penkett, 1977] were assumed in all cases. It has recently been shown that k_1 (298K) is less than 1.5×10^{-15} cm^3 molecule^{-1}s^{-1} [Wine, et al, 1980; Iyer and Rowland, 1980]; hence, Reaction (1) can no longer be considered a viable sink for tropospheric CS_2. Furthermore, recent measurements indicate that CS_2 mixing ratios on the order of 100 pptv are found only in industrialized areas and that background CS_2 levels are 30 pptv or less at ground level [Maroulis and Bandy, 1980] and less than 3 pptv in the free troposphere [Shalaby, et al, 1980]. The large temporal variability in CS_2 found by Maroulis and Bandy [1980] and the sharp CS_2 vertical gradient observed by Shalaby, et al [1980] suggest that the tropospheric lifetime of CS_2 is short — a week or two at most. Hence, an efficient CS_2 removal process other than Reaction (1) must exist.

One possible CS_2 destruction mechanism which warrants consideration is photooxidation:

$$CS_2 \xrightarrow[\lambda > 280\ nm]{h\nu} CS_2^* \qquad (2)$$

$$CS_2^* + O_2 \xrightarrow{k_3} CS + SOO \qquad (3a)$$

$$SOO \xrightarrow{M} SO_2$$

$$CS_2^* + O_2 \xrightarrow{k_3} CS_2 + O_2. \qquad (3b)$$

Evidence for Reaction (3a) was observed in flash photolysis experiments by deSorgo, et al [1965]. Later, Wood and Heicklen [1971], using cw photolysis (313 nm) — end product analysis techniques, deduced that $k_{3a}/k_{3b} \sim .05$. Reaction (3a) was suggested as a possible tropospheric CS_2 sink by Sandalls and Penkett [1977] and by Sze and Ko [1979b]. However, because Reaction (1) was thought to adequately account for CS_2 removal and because experimental data concerning the photooxidation process was sparse, no quantitative evaluation of the potential importance of Reaction (3a) has been carried out. In this communication we present the results of absorption cross section measurements and model calculations which suggest that photooxidation may be an important tropospheric sink for CS_2 and that oxidation of CS, a product of Reaction (3a), may be an important source of OCS.

CS_2 Photoexcitation Rate

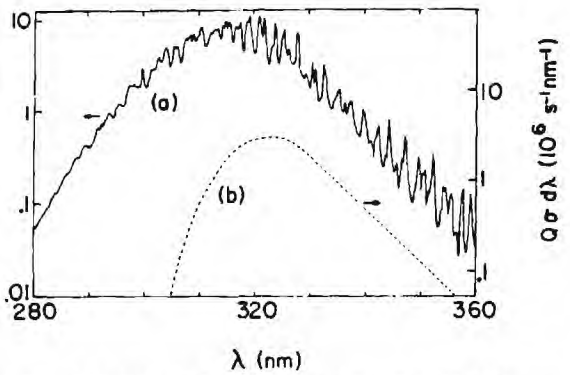
CS_2 absorption cross sections in the 280-360 nm wavelength region have not previously been measured with sufficient accuracy to allow calculation of an accurate tropospheric photoexcitation rate. Hence, we have measured the needed cross sections. Reagent grade CS_2 was vacuum distilled and degased several times before use. Absorption spectra were recorded on a Cary 14 spectrophotometer using a 10 cm brass cell equipped with quartz windows. The spectral resolution was $\sim$ 0.4 nm. Pure CS_2 was used in most runs since it was found that addition of one atmosphere of air did not result in measurable broadening of the spectrum. A majority of the data was obtained using CS_2 pressures of 35 Torr (290-347.5 nm) and 290 Torr (280-297.5 nm and 335-360 nm). Additional pressure dependent data were obtained at a few wavelengths to firmly establish that Beer's law was obeyed over a wide range of [CS_2]. Cross sections were computed at 0.25 nm intervals. Results for T = 298 K are plotted in Figure 1.

Diurnally averaged photoexcitation rates, j_∞, for 30°N latitude at equinox were calculated using a two-stream algorithm to simulate the transfer of solar radiation through an absorbing and multiply scattering atmosphere; optical data were taken from Arveson, et al [1969] and Hudson and Reed [1979]. Very low resolution differential photoexcitation rates (altitude = 0 km) are plotted as a function of wavelength in Figure 1. The computed j_∞ values increase monotonically as a function of altitude from 4.5×10^{-6} s^{-1} at 0 km to 8.9×10^{-5} s^{-1} at 10 km. Thus, the lifetime of CS_2 toward conversion to CS_2* is a few hours. It should be noted that in spite of the short photoexcitation lifetime, the use of diurnally averaged solar flux data is a reasonable approximation because most CS_2* is apparently deactivated by physical quenching [Wood and Heicklen, 1971]. Thus, the lifetime of CS_2 toward photodestruction is probably longer than 1 day.

Many of the strongest features of the CS_2 absorption spectrum are known to result from "hot" bands (i.e., absorption from vibrationally excited CS_2) [Jungen, et al, 1973]. Hence, the possibility exists that j_∞ could be strongly temperature dependent. To explore this possibility absorption spectra were recorded as a function of temperature over the range 250K < T < 325K. Only small differences (on the order of 10%) in the integrated photoexcitation rates were obtained. These differences were ignored in the calculations discussed below.

1. Molecular Sciences Group, Engineering Experiment Station
2. School of Geophysical Sciences

Paper number 1L0725.
0094-8276/81/001L-0725$01.00



g. 1. (a) CS_2 absorption spectrum, T=298K.) Wavelength dependence of the product of the lar flux and the absorption cross section.

tochemical Mechanism

the absence of collisions, the fate of CS_2^* is fluorescence icklen, 1963].

$$CS_2^* \longrightarrow CS_2 + h\nu. \qquad (-2)$$

itation at 337 nm produces two radiating states with times of 2.9 μsec and 17μsec [Brus, 1971; Silvers and Keever, 1976], while excitation at 320 nm produces a single iating state with a lifetime of ~ 15 μsec [Lambert and nbell, 1973]. Fluorescence quenching by N_2 and O_2 has been died by Brus [1971] for 337 nm excitation and by Lambert l Kimbell [1973] for 320 nm excitation. The 2.9 μsec state is nched at a gas kinetic rate by both N_2 and O_2 while the nching rates measured for the longer lived states are in the ge 2-5 × 10^{-11} $cm^3molecule^{-1}s^{-1}$.

The lifetimes and quenching rates discussed above suggest it, under tropospheric conditions, fluorescence is a negligible $_2^*$ removal process as are reactions with atmospheric trace stituents such as O_3. The important processes are Reactions), (3b) and the additional quenching reactions

$$CS_2^* + N_2 \longrightarrow CS_2 + N_2 \qquad (4)$$

$$CS_2^* + H_2O \longrightarrow CS_2 + H_2O. \qquad (5)$$

is not known but is probably near gas kinetic. If the products Reactions (3a), (3b), (4), and (5) are formed directly from S_2^* deactivation (an assumption which has not been verified perimentally) then Wood and Heicklen's results that $k_{3a}/k_{3b} \sim 5$ would, in conjunction with the fluorescence quenching sults, imply a quantum yield for CS + SOO formation under oposphere conditions of .01 – .015.

The fate of CS produced from Reaction 3a is probably action with O_2:

$$CS + O_2 \xrightarrow{k_6} \begin{cases} \longrightarrow OCS + O & (6a) \\ \longrightarrow CO + SO & (6b) \end{cases}$$

k_6 (293K) = 4.5 × 10^{-19} $cm^3molecule^{-1}s^{-1}$ [Richardson, 1975]. he reaction

$$CS + O_3 \xrightarrow{k_7} \begin{cases} \longrightarrow OCS + O_2 & (7a) \\ \longrightarrow SO + CO_2 & (7b) \\ \longrightarrow CO + SO_2 & (7c) \end{cases}$$

would also be important if $k_7 > 1 \times 10^{-12}$ $cm^3molecule^{-1}s^{-1}$ or if $_6$ is significantly slower than Richardson's value. Heterogeneous removal of CS is probably much too slow to be mportant.

The branching ratio k_{6a}/k_{6b} is in question. Richardson [1975] found Reaction (6a) to be the dominant channel, $k_{6a} > 9\ k_{6b}$, while Wood and Heicklen [1971] found $k_{6a} \approx 1.2\ k_{6b}$. Olszyna and Heicklen [1970] report indirect evidence that OCS, CO_2, and CO are formed from Reaction (7) in the ratio 0.555:0.097:0.348. SO formed in Reactions (6b) and (7b) is rapidly oxidized to SO_2:

$$SO + O_2 \longrightarrow SO_2 + O \qquad (8)$$

k_8 (298K) = 9 × 10^{-16} $cm^3molecule^{-1}s^{-1}$ [Baulch, et al, 1980].

Clearly, the relative yields of OCS and SO_2 from CS_2 photooxidation depend critically on the branching ratio for Reaction (6) and, if it is fast enough to be competitive, Reaction (7) as well.

Using the above photochemical scheme and including reaction with OH as an additional loss mechanism for OCS and formation mechanism for SO_2

$$OH + OCS \xrightarrow{k_9} \text{products} \longrightarrow SO_2 \qquad (9)$$

k_9 = 8.8 × 10^{-15} $cm^3molecule^{-1}s^{-1}$ [Ravishankara, et al, 1980], we obtain the following rate equations for CS_2 removal and OCS, SO_2 formation:

$$\text{CS}_2 \text{ loss rate} = \left(\frac{k_{3a}[O_2]}{k_3[O_2] + k_4[N_2] + k_5[H_2O]} \right) j_{a_s}[CS_2] \equiv \Phi_{CS}\, j_{a_s}[CS_2] \qquad (I)$$

$$\text{OCS formation rate} = \Phi_{CS}\, j_{a_s}[CS_2] \left(\frac{k_{6a}[O_2] + k_{7a}[O_3]}{k_3[O_2] + k_7[O_3]} \right)$$

$$\equiv \Phi_{CS}\, j_{a_s}[CS_2]\, \Phi_{OCS} \qquad (II)$$

$$SO_2 \text{ formation rate} = \Phi_{CS}\, j_{a_s}[CS_2](2 - \Phi_{OCS}) + k_9[OH][OCS]. \qquad (III)$$

There is insufficient experimental data available to allow accurate determination of either Φ_{CS} or Φ_{OCS}. Hence, in the calculations discussed below, both parameters were varied over considerable ranges — $0.01 \le \Phi_{CS} \le 0.1$ and $0.1 \le \Phi_{OCS} \le 1.0$. The limits were chosen to bracket the range of reasonable values (based on sparse measurement and laboratory data). While we cannot preclude the possibility that $\Phi_{CS} \le 0.01$, results are not presented for this case because a) the calculated CS_2 profile would be inconsistent with recent measurements [Shalaby, et al, 1980] and b) photooxidation would not be a significant source of OCS.

Model Calculations

To evaluate the potential role of CS_2 photooxidation in tropospheric sulfur chemistry, we have carried out a series of sensitivity calculations using a one-dimensional steady state model, which couples vertical transport and tropospheric photochemistry. Vertical transport was parameterized using the standard eddy diffusion approximation, with a constant diffusion coefficient of 1 × 10^5 $cm^{-2}s^{-1}$. Ambient conditions appropriate for the remote marine atmosphere at a latitude of 30° at equinox were adopted from Oort and Rasmusson [1970] and the U.S. Standard Atmosphere, 1976.

Table I. Model Calculation Parameters

Model No.	Φ_{CS}	Φ_{OCS}	τ_{OCS} (years)
1	0.1	1.0	1
2	0.05	1.0	1
3	0.01	1.0	1
4	0.1	0.1	1
5	0.01	0.1	1
6	0.1	1.0	2

Concentration profiles of CS_2, OCS, and SO_2 were calculated for varying values of Φ_{cs}, Φ_{ocs}, and τ_{ocs} (the OCS atmospheric lifetime) as summarized in Table I. Because the reaction of SO_2 with OH is a major loss pathway for SO_2 [Davis, et al, 1979], calculation of the SO_2 profile requires knowledge of the atmospheric abundance of OH. The OH profile used in our calculation was generated using the model of Chameides and Tan [1981].

The calculated CS_2 profiles illustrated in Figure 2 were obtained by assuming a balance between a surface source, vertical transport, and loss via photooxidation. In all calculations, the CS_2 abundance at 0 km was fixed at 20 pptv. However, we note that the background surface CS_2 concentration has not yet been reliably established, although measurements over North America appear to suggest a value of about 5-30 pptv [Maroulis and Bandy, 1980; Shalaby, et al, 1980]. Since all the sulfur profiles presented here scale linearly with CS_2, our results may be easily modified as future measurements more accurately define the global CS_2 abundance. The surface flux necessary to support the calculated CS_2 profiles was found to range from 9×10^7 to 3.5×10^8 molecules $cm^{-2}s^{-1}$; this flux is equivalent to a global CS_2 source strength of 1.8 to 6.9 teragrams per year.

The major feature of the calculated CS_2 profiles shown in Figure 2 is the rapid decrease in $[CS_2]$ with increasing altitude. This vertical gradient is indicative of the rapid removal of CS_2 by the proposed photooxidation mechanism as CS_2 is transported upward from the surface source. It should be noted that as Φ_{cs} is decreased, thereby increasing the CS_2 photochemical lifetime, the vertical gradient in CS_2 becomes somewhat less pronounced. In this regard, Shalaby, et al's [1980] recent finding that CS_2 levels in the free troposphere were immeasurably small while CS_2 in the boundary layer was about 8-20 pptv, appears to support a value for Φ_{cs} significantly larger than 0.01.

We believe that the CS_2 sink due to photooxidation may be sufficiently rapid to cause the large spatial and temporal variations in CS_2 concentrations observed by Maroulis and Bandy [1980]. Just as the short lifetime of CS_2 due to photooxidation leads to a rapid decrease in CS_2 in the vertical in our one-dimensional simulations, this process can also cause a rapid fall-off in CS_2 levels in the horizontal direction as one travels away from source regions.

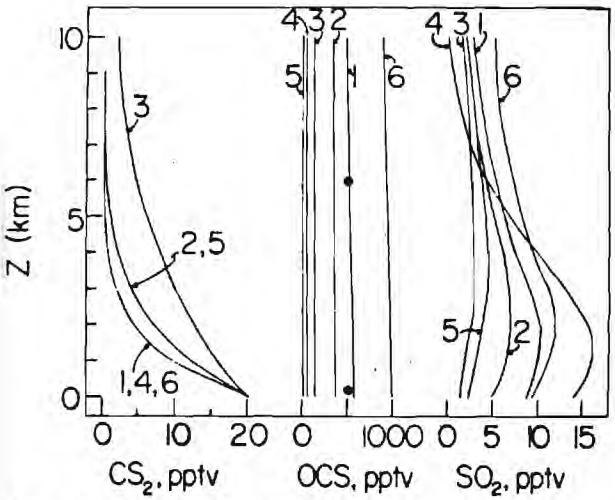


Fig. 2. Calculated (CS_2), (OCS), and (SO_2) altitude profiles. Profile numbers refer to the choice of parameters summarized in Table 1. The filled circles in the OCS plot indicate the averaged OCS levels observed by Torres, et al (1980) in the boundary layer and free troposphere. Note that the only sources of OCS and SO_2 included in these calculations were from CS_2 photooxidation (i.e., Eqn. II) and CS_2 photooxidation (i.e., Eqn. III), respectively.

In the case of OCS, we have, for simplicity, assumed the only source to be via CS_2 photooxidation (i.e., Reactions (2), (3a), and (6a)), while sinks include oceanic hydrolysis [Rowland, 1979] and Reaction (9) with OH. The lifetime of OCS against hydrolysis in the ocean is uncertain and while we have generally adopted a value of one year for this parameter, we have used a value of two years in Model 6 to illustrate the sensitivity of our calculations to the value of this lifetime. Our ability to account for a significant fraction, if not all, of the observed atmospheric OCS abundance (see Figure 2) via CS_2 photooxidation, indicates that this mechanism is potentially a major tropospheric source of OCS. This conclusion, however, is critically dependent upon the assumption that background CS_2 levels are in the 10-20 pptv range and does not preclude the likelihood that other non-photochemical OCS sources [cf. Turco, et al, 1980] also contribute significantly to the global OCS budget. Note that only in Model 5 where both Φ_{cs} and Φ_{ocs} are assigned their minimum values does the calculated OCS mixing ratio (< 10 pptv) become negligible compared to the measured concentrations (~ 500 pptv). On the other hand, in Model 6 we actually calculated more OCS than is observed in the atmosphere.

CS_2 photooxidation appears to be only a minor source for SO_2 in the natural troposphere. The SO_2 profiles illustrated in Figure 2 were obtained by assuming the SO_2 sources were governed by Equation (III) (involving CS_2 photooxidation and OCS oxidation by OH). The sinks for SO_2 included reaction with OH [Atkinson, et al, 1976; Davis, et al, 1979; Harris, et al, 1980], heterogeneous removal with a 5-day lifetime in the boundary layer and a 20-day lifetime in the free troposphere, and loss at the ocean surface with a deposition velocity of 0.5 cm s^{-1} [Liss and Slater, 1974]. As indicated in Figure 2, the CS_2–OCS sources only generate about 1-20 pptv of SO_2 in the boundary layer and 1-10 pptv in the free troposphere. Only if Φ_{cs} is very high and Φ_{ocs} very low can SO_2 levels generated from CS_2 approach the measured concentration of 54 ± 19 pptv in the marine boundary layer [Maroulis, et al, 1980b]. Because of the rapid fall-off in CS_2 levels with altitude, this mechanism cannot (for any combination of Φ_{cs} and Φ_{ocs}) account for a significant fraction of the free tropospheric SO_2 levels of 85 ± 28 pptv measured by Maroulis, et al [1980b].

Conclusions

We conclude from the above analysis that CS_2 photooxidation is probably an important tropospheric sink for the CS_2 giving a lifetime on the order of a week or two. If background CS_2 levels are 10-20 pptv, then CS_2 photooxidation may be an important global source of OCS as well. However, these conclusions are based on rather limited experimental evidence. No direct, real-time kinetic data is available to check the proposed CS_2 photooxidation mechanism. The yields Φ_{cs} and Φ_{ocs}, which are crucial to an assessment of the atmospheric relevance of CS_2 photooxidation, remain poorly defined, as does the tropospheric lifetime of OCS. The dependence of Φ_{cs} on excitation wavelength has not been examined at all. Further investigations aimed at better defining Φ_{cs}, Φ_{ocs}, and τ_{ocs} are needed.

Acknowledgements

This work was supported by the National Science Foundation through Grants No. ATM-78-10092 and ATM-80-19040 (PHW and ARR) and by the National Aeronautics and Space Administration through Grant No. NAG-1-85 (WLC). C. A. Gump and N. M. Kreutter assisted in the absorption cross section measurements. The authors thank Dr. A. R. Bandy for helpful discussions.

References

Arveson, J. C., R. N. Griffin, Jr., and B. D. Pearson, Jr., Determination of extraterrestrial solar spectral irradiance from a research aircraft, Appl. Opt., 11, 2215-2232, 1969.

Atkinson, R., R. A. Perry, and J. N. Pitts, Jr., Rate constants for the reactions of the OH radical with NO_2 (M = Ar and N_2) and SO_2 (M = Ar), J. Chem. Phys., 65, 306-310, 1976.

Baulch, D. L., R. A. Cox, R. F. Hampson, Jr., J. A. Kerr, J. Troe, and R. T. Watson, Evaluated kinetic and photochemical data for atmospheric chemistry, J. Phys. and Chem. Ref. Data, 9, 295-471, 1980.

Brus, L. E., Two exponential decay of 3371Å laser excited CS_2 fluorescence, Chem. Phys. Lett., 12, 116-119, 1971.

Chameides, W. L., and A. Tan, The two-dimensional diagnostic model for tropospheric OH: An uncertainty analysis, J. Geophys. Res., in press, 1981.

Crutzen, P. J., The possible importance of CSO for the sulfate layer of the stratosphere, Geophys. Res. Lett., 3, 73-76, 1976.

Davis, D. D., A. R. Ravishankara, and S. Fischer, SO_2 oxidation via the hydroxyl radical: Atmospheric fate of HSO_3 radicals, Geophys. Res. Lett., 6, 113-116, 1979.

deSorgo, M., A. J. Yarwood, O. P. Strausz, and H. E. Gunning, The photolysis of carbon disulfide and carbon disulfide-oxygen mixtures, Can. J. Chem., 43, 1886-1891, 1965.

Hanst. P. L., L. L. Speller, D. M. Watts, J. W. Spence, and M. F. J. Miller, Infrared measurements of fluorocarbons, carbon tetrachloride, carbonyl sulfide, and other atmospheric trace gases, JAPCA, 25, 1220-1226, 1975.

Harris, G. W., R. Atkinson, and J. N. Pitts, Jr., Temperature dependence of the reaction $OH + SO_2 + M \longrightarrow HSO_3 + M$ for M = Ar and SF_6, Chem. Phys. Lett., 69, 378-382, 1980.

Heicklen, J., The fluorescence of carbon disulfide vapor, J. Amer. Chem. Soc., 85, 3562-3565, 1963.

Iyer, R. S. and F. S. Rowland, A significant upper limit for the rate of formation of OCS from the reaction of OH with CS_2, Geophys. Res. Lett., 7, 797-800, 1980.

Jungen, Ch., D. N. Malm, and A. J. Merer, Analysis of $a^1\Delta_g - {}^1\Sigma_g^+$ transition of CS_2 in the near ultraviolet, Can. J. Phys., 51, 1471-1490, 1973.

Kurylo, M. J., Flash photolysis resonance fluorescence investigation of the reactions of OH radicals with OCS and CS_2, Chem. Phys. Lett., 58, 238-242, 1978.

Lambert, C. and G. H. Kimbell, The fluorescence of CS_2 vapor, Can. J. Chem., 51, 2601-2608, 1973.

Liss, P. S. and P. G. Slater, Flux of gases across the air-sea interface, Nature, 247, 181-182, 1974.

Logan, J. A., M. B. McElroy, S. C. Wofsy, and M. J. Prather, Oxidation of CS_2 and COS: Sources for atmospheric SO_2, Nature, 281, 185-188, 1979.

Maroulis, P. J. and A. R. Bandy, Measurements of atmospheric concentrations of CS_2 in the eastern United States, Geophys. Res. Lett., 7, 681-684, 1980a.

Maroulis, P. J., A. L. Torres, A. B. Goldberg, and A. R. Bandy, Atmospheric SO_2 measurements on project GAMETAG, J. Geophys. Res., 85, 7345-7349, 1980b.

Olszyna, K. J. and J. Heicklen, The reaction of ozone with carbon disulfide, J. Phys. Chem., 74, 4188-4198, 1970.

Oort, A. H. and E. M. Rasmusson, Atmospheric Circulation Statistics, NOAA Prof. Pap. 5, U.S. Gov't. Printing Office, Washington, D.C., 323 pp., 1970.

Ravishankara, A. R., N. M. Kreutter, R. C. Shah, and P. H. Wine, Rate of Reaction of OH with COS, Geophys. Res. Lett., 7, 861-864, 1980.

Richardson, R. J., CS-O_2 flame reaction chemistry, J. Phys. Chem., 79, 1153-1158, 1975.

Rowland, F. S., The atmospheric and ocean sinks for carbonyl sulfide, 4th International Conference of the Commission on Atmospheric Chemistry and Global Pollution, Boulder, Colo., Abstract IV-6, August 1979.

Sandalls, F. J. and S. Penkett, Measurements of carbonyl sulphide and carbon disulphide in the atmosphere, Atmos. Environ., 11, 197-199, 1977.

Shalaby, L., P. J. Maroulis, and A. R. Bandy, Evidence of a short atmospheric lifetime for carbon disulfide, Geophys. Res. Lett., to be submitted, 1981.

Silvers, S. J. and M. R. McKeever, Time and frequency resolution of CS_2 fluorescence excited by a nitrogen laser, Chem. Phys., 18, 333-339, 1976.

Sze, N. D. and M. K. W. Ko, Is CS_2 a precursor for atmospheric COS?, Nature, 278, 731-732, 1979a.

Sze, N. D. and M. K. W. Ko, CS_2 and COS in the stratospheric sulfur budget, Nature, 280, 309-310, 1979b.

Torres, A. L., P. J. Maroulis, A. B. Goldberg, and A. R. Bandy, Atmospheric OCS measurements on project GAMETAG, J. Geophys. Res., 85, 7357-7360, 1980.

Turco, R. P., R. C. Whitten, O. B. Toon, J. B. Pollack, and P. Hamill, OCS, stratospheric aerosols and climate, Nature, 283, 283-286, 1980.

Wine, P. H., R. C. Shah, and A. R. Ravishankara, Rate of reaction of OH with CS_2, J. Phys. Chem., 84, 2499-2503, 1980.

Wood, W. P. and J. Heicklen, The photooxidation of carbon disulfide, J. Phys. Chem., 75, 854-860, 1971.

(Received November 11, 1980;
accepted April 14, 1981.)

APPENDIX C

Preprint of

"Kinetics of OH Reactions with Tropospheric Sulfur Compounds"

KINETICS OF OH REACTIONS WITH TROPOSPHERIC SULFUR COMPOUNDS

P. H. Wine and A. R. Ravishankara
Georgia Institute of Technology
Atlanta, Georgia 30332

1. INTRODUCTION

The tropospheric sulfur cycle has been the subject of intensive investigation in recent years because of the need to assess the contribution of anthropogenically produced sulfur to acid rain, visibility reduction, and climate modification. In most cases, oxidation of sulfur compounds in the troposphere is initiated by OH radical attack. Kinetic data are now available for OH reactions with a number of volatile sulfur compounds. However, all direct studies have been carried out at sub-ambient pressures and/or in the absence of O_2. Only indirect measurements of rate constants have been reported under atmospheric conditions of pressure and gas composition. Two reactions where discrepancies exist between direct measurements and indirect measurements in one atmosphere of air are

$$OH + CH_3SH \rightarrow \text{Products} \qquad (1)$$

and

$$OH + CS_2 \rightarrow \text{Products} . \qquad (2)$$

Cox and Sheppard (1980) have employed a competitive kinetics technique using $OH + C_2H_4$ as the reference reactions ($k_{ref} = 8\times10^{-12}cm^3molecule^{-1}s^{-1}$) to measure k_1 and k_2 in one atm air at 297K. Their result for k_1, $(9.04\pm0.85)\times10^{-11}cm^3molecule^{-1}s^{-1}$, is nearly a factor of three faster than the flash photolysis-resonance fluorescence (FP-RF) results reported by Atkinson, et al (1977) and Wine, et al (1981). Both FP-RF studies employed argon as the buffer gas with $P \leq 120$ Torr. In the case of reaction (2), Cox and Sheppard report $k_2 = (4.3\pm1.6) \times 10^{-13}cm^3molecule^{-1}s^{-1}$; while Wine, et al (1980) and Iyer and Rowland (1980) obtained the results $k_2 \leq 1.5\times10^{-15}$ and $k_2 \leq 3\times10^{-15}$ $cm^3molecule^{-1}s^{-1}$, respectively, under oxygen free conditions with 60 Torr SF_6 (Wine, et al) or 70 Torr CS_2+CO (Iyer and Rowland) buffer gas. The available data for k_1 suggests the importance of a pressure dependent channel under tropospheric conditions. A similar explanation does not seem capable of explaining the much larger difference between measured values for k_2. Burrows and Cox [private communication] have suggested that the existing data for k_2 is consistent with a complex mechanism involving reaction of an initially formed OH-CS_2 complex with O_2. In order to elucidate the mechanisms of reactions (1) and (2) and facilitate proper choice of rate constants for modeling purposes we have undertaken an investigation of the pressure and $[O_2]$ dependence of k_1 and k_2. Simultaneously, we are also studying the pressure and temperature dependence of the rate constant for the reaction

$$OH + SO_2 + M \rightarrow HSO_3 + M, \; M = Ar, N_2, SF_6. \qquad (3)$$

Reaction (3) is now thought to be the dominant homogeneous SO_2 oxidation pathway in both the urban and non-urban troposphere, although it should be pointed out that the potential importance of the CH_3O_2+SO_2 reaction remains a controversial issue [Kan (1981), Sander (1981)].

Some initial results from our studies of reactions (1)-(3) are presented in this paper.

2. EXPERIMENTAL

The flash photolysis-resonance fluorescence technique was employed in all experiments. The application of this technique to the study of OH reactions with atmospheric sulfur compounds has been described in previous publications [Wine (1980,1981); Ravishankara (1980)]. In the present study it was necessary to tailor the spectral distribution of the photoflash so as to produce OH under conditions where the concentrations of other reactive photofragments were small; otherwise secondary reactions involving these photofragments would become dominant. In all experiments where the reaction mixture contained either CS_2 or O_2, OH was produced by 248 nm KrF laser photolysis of H_2O_2 or HNO_3. Some studies of reaction (1) in the absence of O_2 and all investigations of reaction (3) employed broadband flash photolysis of H_2O at wavelengths greater than 165 nm as the source of OH. Over the range of flash energies and species concentrations employed, no evidence for complicating secondary chemistry was observed in the study of reaction (1). However, in the case of reaction (3), both an interfering chemiluminescent signal and secondary production of OH were observed when high SO_2 concentrations were employed Both of these complications resulted from secondary chemistry involving the SO_2 photofragments SO and $O(^3P)$. To suppress the production of these reactive species, the photoflash was filtered with up to 50 Torr-cm SO_2. The SO_2 absorption cross section is smaller than the H_2O cross section over the wavelength range (165-185 nm) where most H_2O photolysis occurs but is very large in the 190-220 nm region. Hence, use of an SO_2 filter resulted in a large decrease in the levels of SO and $O(^3P)$ but only a small decrease in the OH concentration.

Because O_2 quenches OH resonance fluorescence very efficiently, the results reported in this paper are limited to O_2 partial pressures of a few Torr. Modifications in the OH detection technique will be required in order to extend these experiments to O_2 levels typical of the lower troposphere.

The gases used in this study had the following stated purities: CH_3SH > 99.5%, SO_2>99.98%, O_2>99.99%, SF_6>99.99%, and Ar>99.9995%. Both CH_3SH and SO_2 were subjected to repeated freeze (77K)-pump-thaw cycles before use. O_2, SF_6, and Ar were used as supplied. The CS_2 sample was Fischer ACS reagent grade. It was purified by trap-to-trap distillation (210-77K) followed by repeated degasing at 77K.

3. RESULTS AND DISCUSSION

All experiments were carried out under pseudo-first order conditions with the reactant R (R ≡ CH_3SH, CS_2, SO_2) in large excess over OH. Under conditions where OH is removed from the detection zone only by reaction with R, diffusion, and reaction with background impurities and/or the OH photolytic precursor, the OH temporal profile is defined by the relationship

$$[OH]_t = [OH]_o \exp(-k't) \qquad (4)$$

where k' is the pseudo-first order rate constant for OH removal:

$$k' = k_i[R_i] + k_j[P_j] + k_d \ . \qquad (5)$$

In equation (5), k_i is the bimolecular rate constant for reaction of OH with the reactant R_i, k_j is the bimolecular rate constant for the reaction of OH with the photolytic precursor P_j, and k_d is the first order rate constant for removal of OH by diffusion from the field of view of the detector and reaction with background impurities. Both k_i and k_j can depend upon temperature, pressure, and the identity of the buffer gas. For a specified set of $[R_i]$, $[P_j]$, pressure, and temperature, k' is determined from the slope of a $-\ell n S_t$ vs. t plot (S_t ≡ the resonance fluorescence signal at time t). The desired bimolecular rate constant is then determined from the dependence of k' on $[R_i]$ at fixed $[P_j]$, temperature, and pressure.

The results obtained for each reaction are discussed individually below.

OH + CH_3SH → products

The results obtained for reaction (1) are summarized in Table 1. Within experimental uncertainties no dependence of k_1 on pressure or $[O_2]$ is observed. The average of the five rate constants reported in Table 1, $k_1 = 3.18 \times 10^{-11}$ $cm^3 molecule^{-1} s^{-1}$, is in good agreement with the previous FP-RF results of Atkinson, et al (1977) and Wine, et al (1981). Since SF_6 is a more efficient third body than air, the observation of no pressure dependence for k_1 over the range 25-200 Torr SF_6 effectively eliminates the possibility that formation and stabilization of a reaction complex results in k_1 being faster at P = 1 atm than at P ∿ 50 Torr. However, further experiments are needed with various O_2/M mixture before an $[O_2]$ dependence can be definitively rejected as a possibility.

Table 1

Rate constants for the reaction OH+CH_3SH → products. T = 298±1K.

OH Production Mechanism*	Buffer Gas/ Pressure (Torr)	O_2 Partial Pressure (Torr)	$k_1 \pm 2\sigma^\dagger$ (10^{-11} $cm^3 molecule^{-1} s^{-1}$)
1	25/SF_6	0	3.25 ± 0.09
1	200/SF_6	0	3.09 ± 0.10
1	80/Ar	0	3.04 ± 0.19
2	100/Ar	0	3.47 ± 0.12
2	100/Ar	3.0	3.06 ± 0.22

* 1: broadband flash photolysis of H_2O at λ > 165 nm; 2: KrF laser photolysis of HNO_3

† Errors refer to precision only

OH + CS_2 → products

The studies of reaction (2) were extremely signal limited because both CS_2 and O_2 quench OH resonance fluorescence very efficiently. The experiments reported here were aimed primarily at determining qualitatively whether or not the reaction rate is enhanced by the presence of O_2. For this reason SF_6, which is very efficient at stabilizing collision complexes, was employed as the buffer gas in all experiments. In agreement with our earlier study (Wine (1980)], the reaction was found to be very slow in the absence of O_2. When 1-3 Torr O_2 was added to the reaction mixture, a pronounced increase in k_2 was observed. k_2 was also found to increase with decreasing temperature; this suggests that the initial step in the reaction mechanism is formation of an OH...CS_2 complex.

Table 2

Rate constants for the reaction OH+CS_2 → products. The buffer gas was SF_6 in all experiments. OH was produced by KrF laser photolysis of H_2O_2.

T(K)	P(Torr)	P_{O_2} (Torr)	$k_2 \pm 2\sigma^\dagger$ (10^{-15} $cm^3 molecule^{-1} s^{-1}$)
298	100	0	< 1
298	250	0	< 5
298	250	1.2	29 ± 4
298	250	3.3	51 ± 17
298	500	1.0	32 ± 7
259	250	0	7 ± 3
259	250	1.2	110 ± 50

† Errors refer to precision only

OH + SO_2 → products

At this time we have completed a study of the temperature and pressure dependence of k_3 for M = SF_6. The results are summarized in Table 3. Calvert, et al (1978) reviewed the data base available at the time and recommended a value of 1.1×10^{-12} $cm^3 molecule^{-1} s^{-1}$ for k_3 at 298K and 1 atm air. Since then, new data have been reported by Davis, et al (1979) and Harris, et al (1980);

these data suggest a slightly lower value for k_3 —in the range 9-10 x 10^{-13} $cm^3 molecule^{-1} s^{-1}$. Our results for M = SF_6 are typically ∿ 20% lower than those reported by Harris, et al, and thus suggest a value of ∿ 8 x 10^{-13} $cm^3 molecule^{-1} s^{-1}$ for k_3 at 298K and 1 atm air. Further experiments with M = Ar and N_2 are in progress.

Table 3

Rate constants for the reaction $OH+SO_2+SF_6$. Units are 10^{-13} $cm^3 molecule^{-1} s^{-1}$; Errors are 2σ and represent precision only.

$[SF_6]$ / 10^{17} molecule cm^{-3} \ T(K)	260	300	360	420
5.0	2.96 ± 0.11	1.92 ± 0.20	1.29 ± 0.09	1.07 ± 0.04
10.0	3.70 ± 0.30	2.97 ± 0.13	2.18 ± 0.17	1.51 ± 0.11
20.0	5.68 ± 0.46	4.38 ± 0.35	2.63 ± 0.30	2.19 ± 0.15
40.0	7.31 ± 0.60	5.27 ± 0.15	4.38 ± 0.24	3.71 ± 0.41
80.0	9.50 ± 0.86	7.17 ± 0.30	5.83 ± 0.33	4.91 ± 0.50
160	12.4 ± 1.4	9.66 ± 0.80	7.45 ± 0.85	7.19 ± 0.70

4. CONCLUSIONS

The following conclusions can be drawn from the results presented in this paper:

(1) k_1 is independent of pressure if the buffer gas is chemically inert (i.e. Ar, N_2, or SF_6 but not necessarily O_2).
(2) Reaction (2) becomes much faster when a few Torr O_2 are added to the reaction mixture. The large difference in rate constants reported by Cox and Sheppard (1980) vs. Wine, et al (1980) and Iyer and Rowland (1980) appears to be attributable to the dependence of k_2 on $[O_2]$.
(3) Reaction (3) appears to be a little slower under atmospheric conditions than current evaluations suggest.

Quantitative assessment of the $[O_2]$ dependence of k_1 and k_2 (and for that matter, k_3 as well) at O_2 levels found in the troposphere will require vast improvement in OH detection sensitivity. An apparatus featuring pulsed laser induced fluorexcence detection of OH is being constructed in our laboratory, and is expected to be "on line" soon. This apparatus provides the sensitivity needed to monitor OH kinetically under the desired conditions.

5. ACKNOWLEDGEMENTS

We would like to thank D. H. Semmes and C. A. Gump for assisting with some of the experiments. This work was supported by the National Science Foundation under grant No. ATM-80-19040.

6. REFERENCES

Atkinson, R., R. A. Perry, and J. N. Pitts, Jr., 1977: Rate constants for the reaction of the OH radical with CH_3SH and CH_3NH_2 over the temperature range 299-426K. J. Chem. Phys., 66, 1578-1581.

Calvert, J. G., F. Su, J. W. Bottenheim and O. P Strausz, 1978; Mechanism of the homogeneous oxidation of sulfur dioxide in the troposphere. Atmos. Environ., 12, 197-226.

Cox, R. A. and D. Sheppard, 1980: Reactions of OH radicals with gaseous sulfur componds, Nature, 284, 330-331.

Davis, D. D., A. R. Ravishankara and S. Fischer, 1979: SO_2 oxidation via the hydroxyl radical: atmospheric fate of HSO_x radicals. Geophys. Res. Lett., 6, 113-116.

Harris, G. W., R. Atkinson and J. N. Pitts, Jr., 1980: Temperature dependence of the reaction $OH+SO_2+M \rightarrow HSO_3+M$ for M = Ar and SF_6. Chem. Phys. Lett., 69, 378-382.

Iyer, R. S. and F. S. Rowland, 1980: A significant upper limit for the rate of formation of OCS from the reaction of OH with CS_2. Geophys. Res. Lett., 7, 797-800.

Kan, C. S., J. G. Calvert and J. H. Shaw, 1981: Oxidation of sulfur dioxide by methylperoxy radicals. J. Phys. Chem., 85, 1126-1132.

Ravishankara, A. R., N. M. Kreutter, R. C. Shah and P. H. Wine, 1980: Rate of reaction of OH with COS. Geophys. Res. Lett., 7, 861-864.

Sander, S. P. and R. T. Watson, 1981: A kinetics study of the reaction of SO_2 with CH_3O_2. Chem. Phys. Lett., 77, 473-475.

Wine, P. H., R. C. Shah and A. R. Ravishankara, 1980: Rate of reaction of OH with CS_2. J. Phys. Chem., 85, 2499-2503

Wine, P. H., N. M. Kreutter, C. A. Gump and A. R. Ravishankara, 1981: Kinetics of OH reactions with the atmospheric sulfur compounds H_2S, CH_3SH, CH_3SCH_3, and CH_3SSCH_3. J. Phys. Chem., 85, 2660-2665.

PROGRESS REPORT

I. Work Completed during the period 1/81 - 5/82

During the first 17 months of our current NSF grant, we have focused our attention mainly on tropospheric sulfur chemistry. Four separate studies have been completed and are described below:

(1) The flash photolysis-resonance fluorescence technique was employed to study the kinetics of OH radical reactions with $H_2S(k_1)$, $CH_3SH(k_2)$, $CH_3SCH_3(k_3)$, and $CH_3SSCH_3(k_4)$ over the temperature range 244 - 367 K. A manuscript which describes this work, compares the results with previous investigations, and discusses the atmospheric implications of the results was recently published in the Journal of Physical Chemistry; a copy of the manuscript is attached as Appendix I.

(2) Electronically excited $CS_2(CS_2^*)$ was shown to be rapidly produced in the troposphere by absorption of sun light (lifetime of CS_2 toward conversion to CS_2^* at midday is a few hours). It was shown that the reaction of CS_2^* with O_2 can remove tropospheric CS_2 on a time scale of one or two weeks if the CS + SOO yield from this reaction is greater than 0.01. Calculations indicated that the photooxidation mechanism can be a major source of tropospheric COS but only a minor source of SO_2. A manuscript describing this study was recently published in Geophysical Research Letters; a copy is attached as Appendix II. Further direct real time studies of the important photooxidation reactions are included in our new proposal.

(3) The reactions of OH radicals with $CH_3SH(k_2)$ and $CS_2(k_5)$ were reinvestigated over a much broader range of experimental conditions than were employed in our previous studies[1,2]. k_2 was found to be independent of pressure in the presence of chemically inert buffer gases, i.e. Ar and

SF_6, and also independent of $[O_2]$ at O_2 partial pressures up to a few Torr. Hence, the fast rate constant measured by Cox and Sheppard[3] in 1 atm air, which is a factor of three faster than obtained in our study or a similar study by Atkinson, et al.,[4] cannot be attributed to differences in the pressure regimes of the studies. k_5 was found to increase significantly when a few Torr of O_2 were added to the reaction mixture at higher pressures. The large differences in rate constants reported by Cox and Sheppard[3] vs. Wine, et al,[2] Iyer and Rowland,[5] and Leu and Smith,[6] appear to be attributable to the dependence of k_5 on $[O_2]$. A paper describing these results was presented at the Second Symposium on the Composition of the Nonurban Troposphere, Williamsburg, Va. in May 1982. The preprint for this paper was published in the conference proceedings by the American Meteorological Society and is attached as Appendix III. Extension of the above measurements to atmospheric O_2 levels requires considerable improvement in OH detection sensitivity and is currently being worked on. If a recent indirect study by Jones, et al.[7] is correct, the OH + CS_2 + O_2 interaction is a major source of tropospheric COS.

(4) The kinetics of the important combination reaction OH + SO_2 + M → HSO_3 + M have been investigated as a function of pressure (M = He, Ar, N_2, SF_6) and temperature (M = Ar and SF_6). The flash photolysis-resonance fluorescence technique was employed with OH produced by photolysis of H_2O. Two important experimental features were 1) direct measurement of the SO_2 concentration in the slow flow system by UV photometry and 2) elimination of complications resulting from photolytic production of SO and $O(^3P)$ through use of an SO_2 filter between the flashlamp and the reaction cell. We find the reaction to be somewhat slower than previously believed. Our

results suggest a rate constant of 8×10^{-13} cm^3 $molecule^{-1}$ s^{-1} at 1 atm N_2 and 298 K. Recommended rate constants based on earlier results are in the range $9\text{-}12 \times 10^{-13}$ cm^3 $molecule^{-1}$ s^{-1} [8-10]. A manuscript describing this work will be submitted to the Journal of Physical Chemistry in the near future. A collection of Figures and Tables which summarize the experimental results are attached as Appendix IV.

In addition to the above mentioned research in tropospheric sulfur chemistry, we have investigated the kinetics of chlorine atom reactions with a series of chlorosubstituted ethanes. This work (supported partially by NASA and partially by NSF) was motivated by the realization that reaction with $Cl(^2P)$ could be an important sink for methyl chloroform (CH_3CCl_3) in the upper troposphere and lower stratosphere if the rate constant for the reaction was greater than 1×10^{-12} cm^3 $molecule^{-1}$ s^{-1}. We found the reaction to be surprisingly slow. The kinetics of $Cl(^2P)$ reactions with CH_3CH_2Cl, CH_2ClCH_2Cl, CH_3CHCl_2, and $CH_2ClCHCl_2$ were investigated in order to gain insight into the lack of reactivity observed in the case of the $Cl(^2P) + CH_3CCl_3$ reaction (at ambient temperatures and below $Cl(^2P)$ reacts with ethane several thousand times faster than with methyl chloroform). A manuscript describing the $Cl(^2P) + CH_3CCl_3$ study has been accepted for publication in Chemical Physics Letters; a preprint is attached as Appendix V. A manuscript describing our investigations of the remaining reactions will be submitted to the Journal of Physical Chemistry in the near future. A paper describing this work was presented at the 15th Informal Conference on Photochemistry at Stanford University in June 1982. The abstract for this paper is attached as Appendix VI.

II. Plans for the remainder of the current grant period (6/82 - 12/82)

In order to extend our measurements of k_2 (OH + CH_3SH) and k_5 (OH + CS_2) to atmospheric conditions of pressure and [O_2], a new apparatus featuring pulsed laser induced fluorescence detection of OH has been constructed. This apparatus will be used extensively on our newly proposed research program and therefore is described in detail in a later section. At this time, we can report that preliminary kinetic data has been obtained which demonstrates a very large improvement in OH detection sensitivity over that obtained in our conventional flash photolysis-resonance fluorescence system. The experiments to be carried out with the new apparatus require that the rare gas halide photolysis laser run at a relatively high repetition rate (5 Hz) for extended periods of time. Hence, it has become necessary to install a gas circulation system which continuously removes impurities and injects new halogen "fuel". This system has been ordered and should be on-line by August. We expect to complete our study of the [O_2] dependence of k_2 and k_5 before the end of the current grant period.

A major uncertainty in hydrocarbon oxidation chemistry results from the paucity of data concerning the rates and mechanisms of the vapor phase methylhydroperoxide removal processes and the extent to which these processes compete with heterogeneous removal:

$$CH_3OOH \longrightarrow \text{products} \qquad \text{(a)}$$

$$CH_3OOH + OH \longrightarrow \text{products}, \qquad \text{(b)}$$

Studies of reactions (a) and (b) are currently in progress and should be completed before the end of the current grant period. We are in the process

of checking the absorption cross-sections reported by Molina and Arguello[11] at several wavelengths, determining the primary photolysis products as a function of wavelength, measuring k_b as a function of temperature, and by observing NO_2 formation in the presence of added NO, measuring the yield of CH_3O_2 from reaction (b). In addition to reaction (b), our originally proposed work in the area of hydrocarbon oxidation chemistry included a study of the reaction $CH_3O + O_2 \longrightarrow CH_2O + H_2O$. However, since a recent direct measurement of the temperature dependence of this reaction rate using a technique identical to the one we proposed is in good agreement with earlier indirect measurements and demonstrates conclusively that reaction with O_2 is the dominant CH_3O removal mechanism in the atmosphere, another study of CH_3O reactions now seems less important than the other systems under study in our laboratory.

Chameides and Davis[13] recently proposed that iodine catalytic cycles could play an important role in tropospheric chemistry. However, recent measurements[14] indicate that the atmospheric concentration of the proposed iodine photolytic precursor, CH_3I, is considerably lower than Chameides and Davis had projected. The measurement data leads to the conclusion that the CH_3I flux into the troposphere is not sufficient to support the proposed iodine photochemistry unless there exists a CH_3I sink which is at least competitive with photolysis ($\tau \sim 5$ days). We plan to investigate the kinetics of the reaction

$$\mathrm{OH + CH_3I} \begin{cases} \longrightarrow \mathrm{CH_2I + H_2O} & (c_1) \\ \longrightarrow \mathrm{CH_3 + HOI} & (c_2) \end{cases}$$

in order to assess its possible role as a methyl iodide sink. OH reactions with CH_3Cl and CH_3Br are relatively slow ($k \sim 3 \times 10^{-14}$ cm^3 $molecule^{-1}$ s^{-1} at 298 K). However, the channel leading to production of CH_3 + HOX is endothermic for X = Cl, Br whereas this channel may be energetically assessible for X = I (the heat of formation of HOI is not well known but estimates suggest that reaction (c_2) should be about thermoneutral). In order to compete with photolysis as a CH_3I removal process, reactions (c) must proceed with $k \sim 1 \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1}; if such a rate constant is observed, then the reaction of OH with CD_3I will also be investigated in order to obtain some information about the branching ratio for channels (c_1) and (c_2).

References:

1. P.H. Wine, N.M. Kruetter, C.A. Gump, and A.R. Ravishankara, J. Phys. Chem. 85, 2660 (1981), Appendix I.

2. P.H. Wine, R.C. Shah, and A.R. Ravishankara, J. Phys. Chem. 84, 2499 (1980).

3. R.A. Cox and D. Sheppard, Nature 284, 330 (1980).

4. R. Atkinson, R.A. Perry, and J.N. Pitts, Jr., J. Chem. Phys. 66, 1578 (1977).

5. R.S. Iyer and F.S. Rowland, Geophys. Res. Lett. 7, 797 (1980).

6. M.T. Leu and R.H. Smith, J. Phys. Chem. 86, 958 (1982).

7. B.M.R. Jones, J.P. Burrows, R.A. Cox, and S.A. Penkett, Chem. Phys. Lett. 88, 372 (1982).

8. G.W. Harris, R. Atkinson, and J.N. Pitts, Jr., Chem. Phys. Lett. 69, 378 (1980).

9. J.G. Calvert, F. Su, J.W. Bottenheim, and O.P. Strausz, Atmos. Environ. 12, 197 (1978).

10. D.D. Davis, A.R. Ravishankara, and S. Fischer, Geophys. Res. Lett. 6, 113 (1979).

11. M.J. Molina and G. Arguello, Geophys. Res. Lett. 6, 953 (1979).

12. D. Gutman, N. Sanders, and J.E. Butler, J. Phys. Chem. 86, 66 (1982).

13. W.L. Chameides and D.D. Davis, J. Geophys. Res. 85, 7383 (1980).

14. R.A. Rasmussen, M.A.K. Khalil, R. Gunawardena, and S.D. Hoyt, J. Geophys. Res. 87, 3078 (1982).

APPENDIX VI

NATIONAL SCIENCE FOUNDATION
Washington, D.C. 20550

FINAL PROJECT REPORT
NSF FORM 98A

PLEASE READ INSTRUCTIONS ON REVERSE BEFORE COMPLETING

PART I–PROJECT IDENTIFICATION INFORMATION

1. Institution and Address	2. NSF Program	3. NSF Award Number
Georgia Institute of Technology Atlanta, GA 30332	Atmospheric Sciences	ATM-80-19040
	4. Award Period From 12/15/80 To 5/31/83	5. Cumulative Award Amount $122,766

6. Project Title

A Kinetics Investigation of Several Key Tropospheric Chemical Reactions

PART II–SUMMARY OF COMPLETED PROJECT *(FOR PUBLIC USE)*

This project was aimed at improving our current understanding of tropospheric chemistry through careful measurement of a number of key reaction rates. The experimental approach involved variations of the flash photolysis-resonance fluorescence technique.

Major emphasis was placed on investigating the important oxidation initiation reactions of hydroxyl radicals with tropospheric sulfur compounds. Reactions which were studied include those of OH with SO_2, CS_2, H_2S, CH_3SH, CH_3SCH_3, and CH_3SSCH_3. Variation of reaction rates with temperature, pressure, and, in some cases, O_2 partial pressure was investigated. Important findings include direct measurement of O_2 enhancement of the OH + CS_2 reaction rate and discovery that OH reactions with SO_2 and CH_3SCH_3 are somewhat slower than previously believed. Also, we demonstrated the potential role of photooxidation via an excited electronic state as a pathway for CS_2 oxidation in the troposphere. Our study of the OH + SO_2 reaction was by far the most comprehensive to date.

Because of its possible role as a sink for CH_3CCl_3 in the upper troposphere and lower stratosphere, the reaction Cl + CH_3CCl_3 → CH_2CCl_3 + HCl was studied. This reaction was found to be surprisingly slow--at least 1300 times slower than the Cl + CH_3CH_3 reaction. To gain some insight into the observed lack of reactivity, Cl reactions with other chloro-substituted ethanes were also investigated. Cl substitution at carbon "a" appears to weaken remaining C-H bonds on carbon "a" but strengthen C-H bonds on carbon "b".

PART III–TECHNICAL INFORMATION *(FOR PROGRAM MANAGEMENT USES)*

1. ITEM *(Check appropriate blocks)*	NONE	ATTACHED	PREVIOUSLY FURNISHED	TO BE FURNISHED SEPARATELY TO PROGRAM	
				Check (✓)	Approx. Date
a. Abstracts of Theses	X				
b. Publication Citations		X			
c. Data on Scientific Collaborators		X			
d. Information on Inventions	X				
e. Technical Description of Project and Results		X			
f. Other *(specify)*					

2. Principal Investigator/Project Director Name *(Typed)*	3. Principal Investigator/Project Director Signature	4. Date
Paul H. Wine A. R. Ravishankara	Paul H. Wine	4/ 6/83

NSF Form 98A (5-78) Supersedes All Previous Editions

Form Approved OMB No. 99R0013

Publication Citations

(1) "Potential Role of CS_2 Photooxidation in Tropospheric Sulfur Chemistry"
P. H. Wine, W. L. Chameides, and A. R. Ravishankara, Geophysical Research Letters, Volume 8, pages 543-546, May, 1981.

(2) "Kinetics of OH Reactions with the Atmospheric Sulfur Compounds H_2S, CH_3SH, CH_3SCH_3, and CH_3SSCH_3"
P. H. Wine, N. M. Kreutter, C. A. Gump, and A. R. Ravishankara
Journal of Physical Chemistry, Volume 85, pages 2660-2665, September, 1981.

(3) "Kinetics of OH Reactions with Tropospheric Sulfur Compounds"
P. H. Wine and A. R. Ravishankara
2nd Symposium on the Composition of the Nonurban Troposphere, Williamsburg, VA, May, 1982, paper 9.1.

(4) "Upper Limit for the Rate of Reaction of $Cl(^2P_J)$ with Methyl Chloroform"
P. H. Wine, D. H. Semmes, and A. R. Ravishankara
Chemical Physics Letters, Volume 90, pages 128-132, July, 1982.

(5) "Kinetics of $Cl(^2P_J)$ Reactions with the Chloroethanes CH_3CH_2Cl, CH_3CHCl_2, CH_2ClCH_2Cl, and $CH_2ClCHCl_2$"
P. H. Wine and D. H. Semmes
Journal of Physical Chemistry, Volume 87, pages xxxx-xxxx, June, 1983.

(6) "Kinetics of the Reaction $OH + SO_2 + M \rightarrow HSO_3 + M$. Temperature and Pressure Dependence"
P. H. Wine, D. H. Semmes, R. J. Thompson, C. A. Gump, A. R. Ravishankara, A. Torabi, and J. M. Nicovich
To be submitted to the Journal of Physical Chemistry.

Scientific Collaborators

Name	Title
Paul H. Wine (Co-PI)	Senior Research Scientist
A. R. Ravishankara (Co-PI)	Senior Research Scientist
John M. Nicovich	Research Scientist I
Abbas Torabi	Graduate Student
David H. Semmes	Student Assistant
Robert J. Thompson	Student Assistant
Norman M. Kreutter	Student Assistant
Cheryl A. Gump	Student Assistant

Technical Summary

Much of the work carried out with support from grant no. ATM-80-19040 was in the area of tropospheric sulfur chemistry. Four separate studies were completed and are described below:

(1) The flash photolysis-resonance fluorescence technique was employed to study the kinetics of OH radical reactions with H_2S, CH_3SH, CH_3SCH_3, and CH_2SSCH_3 over the temperature range 244-367 K. A manuscript which describes this work, compares the results with previous investigations, and discusses the atmospheric implications of the results was published in the Journal of Physical Chemistry in September of 1981. A copy of the manuscript is attached as Appendix I.

(2) Electronically excited $CS_2(CS_2^*)$ was shown to be rapidly produced in the troposphere by absorption of sunlight (lifetime of CS_2 toward conversion fot CS_2^* at midday is a few hours). It was shown that the reaction of CS_2^* with O_2 can remove tropospheric CS_2 on a time scale of one or two weeks if the CS + SOO yield from this reaction is greater than 0.01. Calculations indicated that the photooxidation mechanism can be a major source of tropospheric COS but only a minor source of SO_2. A manuscript describing this study was published in Geophysical Research Letters in May of 1981. A copy is attached as Appendix II.

(3) The reactions of OH radicals with $CH_3SH(k_1)$ and $CS_2(k_2)$ were reinvestigated over a much broader range of experimental conditions than were employed in our previous studies.[1,2] k_1 was found to be independent of pressure

in the presence of chemically inert buffer gases, i.e. Ar and SF_6, and also independent of $[O_2]$ at O_2 partial pressures up to a few Torr. Hence, the fast rate constant measured by Cox and Sheppard[3] in 1 atm air, which is a factor of three faster than obtained in our study or a similar study by Atkinson, et al.,[4] cannot be attributed to differences in the pressure regimes of the studies. k_2 was found to increase significantly when a few Torr of O_2 were added to the reaction mixture at higher pressures. The large differences in rate constants reported by Cox and Sheppard,[3] Jones, et al.,[5] and Barnes, et. al.,[6] vs. Wine, et al.,[2] Iyer and Rowland,[7] and Leu and Smith,[8] appear to be attributable to the dependence of k_2 on $[O_2]$. Recent indirect studies[5,6] strongly suggest that the OH + CS_2 + O_2 interaction is a major source of tropospheric COS. A paper describing our results was presented at the 2nd Symposium on the Composition of the Nonurban Troposphere in May of 1982. The abstract is attached as Appendix III. Extension of our "direct" measurements to atmospheric O_2 levels requires considerable improvement in OH detection sensitivity and is currently being worked on.

(4) The kinetics of the important combination reaction $OH+SO_2+M \rightarrow HSO_3 + M$ were investigated as a function of pressure (M = He, Ar, N_2, SF_6) and temperature (M = Ar and SF_6). The flash photolysis--resonance fluorescence technique was employed with OH produced by photolysis of H_2O. Two important experimental features were 1) direct measurement of the SO_2 concentration in the flow system by UV photometry and 2) elimination of complications resulting from photolytic production of SO and $O(^3P)$ through use of an SO_2 filter between the flash lamp and the reaction cell. We find the reaction to be somewhat slower than previously believed. Our results suggest a rate constant of 8×10^{-13} cm^3 $molecule^{-1}$ s^{-1} at 1 atm N_2 and 298 K. Recommended rate constants based on earlier results

are in the range 9-12 x 10^{-13} cm^3 $molecule^{-1}$ s^{-1} [9-11] A manuscript describing this work will be submitted to the Journal of Physical Chemistry in the near future. A collection of Figures and Tables which summarize the experimental results is attached as Appendix IV.

In addition to the above mentioned research in tropospheric sulfur chemistry, we have also investigated the kinetics of chlorine atom reactions with a series of chlorosubstituted ethanes. This work (supported partially by NASA and partially by NSF) was motivated by the realization that reaction with $Cl(^2P)$ could be an important sink for methyl chloroform (CH_3CCl_3) in the upper troposphere and lower stratosphere if the rate constant for the reaction was greater than 1 x 10^{-12} cm^3 $molecule^{-1}$ s^{-1}. We found the reaction to be surprisingly slow--at 298K $Cl(^2P)$ reacts with ethane at least 1300 times more rapidly than with methyl chloroform. A manuscript describing the $Cl(^2P)$ + CH_3CCl_3 study was published in Chemical Physics Letters in July of 1982. A reprint is attached as Appendix V. In order to gain insight into the lack of reactivity observed in the case of the $Cl(^2P)$ + CH_3CCl_3 reaction, we also investigated the kinetics of $Cl(^2P)$ + RHCl reactions for RHCl = CH_3CH_2Cl, CH_2ClCH_2Cl, CH_3CHCl_2, and $CH_2ClCHCl_2$. In these studies, secondary production of $Cl(^2P)$ was observed (under some conditions) which could be attributed to the reactions of RCl + Cl_2 → RCl_2 + $Cl(^2P)$. Modelling the observed temporal profiles allowed kinetic data to be obtained for both the $Cl(^2P)$ + RHCl reactions and the RCl + Cl_2 reactions. A manuscript describing these experiments and discussing the observed reactivity trends has been accepted for publication in the Journal of Physical Chemistry and will be published in June, 1983. A preprint is attached as Appendix VI.

References

1. P. H. Wine, N. M. Kreutter, C. A. Gump, and A. R. Ravishankara, J. Phys. Chem. 85, 2660 (1981), Appendix I.

2. P. H. Wine, R. C. Shah, and A. R. Ravishankara, J. Phys. Chem. 84, 2499 (1980).

3. R. A. Cox and D. Sheppard, Nature 284, 330 (1980).

4. R. Atkinson, R. A. Perry, and J. N. Pitts, Jr., J. Chem. Phys. 66, 1578 (1977).

5. B. M. R. Jones, J. P. Burrows, R. A. Cox, and S. A. Penkett, Chem. Phys. Lett. 88, 372 (1982).

6. I. Barnes, K. H. Becker, E. H. Fink, A. Reiner, F. Zabel, and H. Niki, Int. J. Chem. Kinet., in press.

7. R. S. Iyer and F. S. Rowland, Geophys. Res. Lett. 7, 797 (1980).

8. M. T. Leu and R. H. Smith, J. Phys. Chem. 86, 958 (1982).

9. G. W. Harris, R. Atkinson, and J. N. Pitts, Jr., Chem. Phys. Lett. 69, 378 (1980).

10. J. G. Calvert, F. Su, J. W. Bottenheim, and O. P. Strausz, Atmos. Environ. 12, 197 (1978).

11. D. D. Davis, A. R. Ravishankara, and S. Fischer, Geophys. Res.Lett. 6, 113 (1979).

APPENDIX I

Reprint of the Paper

KINETICS OF OH REACTIONS WITH THE ATMOSPHERIC SULFUR COMPOUNDS H_2S, CH_3SH, CH_3SCH_3 and CH_3SSCH_3

Kinetics of OH Reactions with the Atmospheric Sulfur Compounds H_2S, CH_3SH, CH_3SCH_3, and CH_3SSCH_3

P. H. Wine,* N. M. Kreutter, C. A. Gump, and A. R. Ravishankara*

Molecular Sciences Group, Engineering Experiment Station, Georgia Institute of Technology, Atlanta, Georgia 30332
(Received: April 10, 1981; In Final Form: June 1, 1981)

The flash photolysis–resonance fluorescence technique has been employed to study the kinetics of hydroxyl radical reactions with H_2S (k_1), CH_3SH (k_2), CH_3SCH_3 (k_3), and CH_3SSCH_3 (k_4) over the temperature range 244–367 K. The following Arrhenius expressions adequately describe the measured rate constants as a function of temperature (units are cm^3 $molecule^{-1}$ s^{-1}): $k_1 = (6.4 \pm 1.3) \times 10^{-12} \exp[(-55 \pm 58)/T]$; $k_2 = (1.15 \pm 0.39) \times 10^{-11} \exp[(+338 \pm 100)/T]$; $k_3 = (6.8 \pm 1.1) \times 10^{-12} \exp[(-138 \pm 46)/T]$; $k_4 = (5.9 \pm 3.3) \times 10^{-11} \exp[(+380 \pm 160)/T]$. The results are compared with previous investigations, and their implications regarding reaction mechanisms and atmospheric sulfur chemistry are discussed.

Introduction

The atmospheric sulfur cycle has been the subject of intensive investigation in recent years because of the need to assess the contribution of anthropogenically produced sulfur to acid rain, visibility reduction, and climate modification. In heavily industrialized regions such as the eastern United States and western Europe, anthropogenic sulfur emissions exceed natural emissions by 1 order of magnitude.[1] On a global scale, however, natural sulfur emissions are thought to approximately equal those from anthropogenic sources.[2,3] Prediction of adverse effects which may result from anthropogenic sulfur emissions thus requires an understanding of the natural sulfur cycle.

Biological reduction of sulfur compounds is generally believed to be a major natural source of atmospheric sulfur.[2-4] A number of reduced sulfur compounds have been detected in the atmosphere including COS (carbonyl sulfide), CS_2 (carbon disulfide), H_2S (hydrogen sulfide), CH_3SH (methyl mercaptan), CH_3SCH_3 (dimethyl sulfide), and CH_3SSCH_3 (dimethyl disulfide).[5]

With the probable exception of COS and CS_2, atmospheric degradation of reduced sulfur compounds is believed to be initiated by reaction with OH radicals:

$$OH + H_2S \xrightarrow{k_1} SH + H_2O \quad (1)$$

$$OH + CH_3SH \xrightarrow{k_2} \text{products} \quad (2)$$

$$OH + CH_3SCH_3 \xrightarrow{k_3} \text{products} \quad (3)$$

$$OH + CH_3SSCH_3 \xrightarrow{k_4} \text{products} \quad (4)$$

The initial step in understanding the atmospheric chemistry of reduced sulfur species is to accurately establish the rates of reactions 1–4 over the tropospheric temperature range. $k_1(T)$–$k_4(T)$ can be used in conjunction with measured and/or calculated OH concentrations to obtain atmospheric residence times. Where concentration data are available (i.e., H_2S and CH_3SCH_3) source strengths can be computed from known residence times and loss rates.

Some kinetic data are reported in the literature for each of the reactions 1–4, with reaction 1 being the most studied and reaction 4 the least studied. Direct measurements of k_1 have been reported by several investigators using both flash photolysis[6-8] and discharge flow[9,10] techniques. k_1(298 K) values range from 3.1×10^{-12} to 5.5×10^{-12} cm^3 $molecule^{-1}$ s^{-1} while the reported activation energies range from 0 to 880 kcal/mol. Leu and Smith[10] report a non-Arrhenius temperature dependence with $k_1(T)$ going through a minimum in the range 265–300 K. The data of Michael et al.[8] support this unusual temperature dependence although these authors point out that a temperature-independent k_1 would also be consistent with their data. The only direct measurement of k_2, a flash photolysis–resonance fluorescence study by Atkinson et al.,[11] reports $k_2 = 8.9 \times 10^{-12} \exp(+400/T)$ cm^3 $molecule^{-1}$ s^{-1} for $299 < T < 426$ K. There have been two flash photolysis–resonance fluorescence studies of reaction 3 which are in excellent agreement,[12,13] the combined results giving $k_3 = 6.1 \times 10^{-12} \exp(+134/T)$ for $273 < T < 426$ K. No direct measurements of k_4 have been reported. In addition to the above results, indirect determinations of rate constants for reactions 1–4 at 297 K have been reported by Cox and Sheppard.[14] These investigators measured k_1–k_4 relative to the rate constant for the reaction of OH with ethylene (assumed to be 8.0×10^{-12} cm^3 $molecule^{-1}$ s^{-1}) and obtained $k_1 = 5.0 \times 10^{-12}$, $k_2 = 9.0 \times 10^{-11}$, $k_3 = 9.1 \times 10^{-12}$, and $k_4 = 2.2 \times 10^{-10}$ cm^3 $molecule^{-1}$ s^{-1}. It is clear that only in the case of k_3 is there good agreement of several independent studies. Furthermore, very few data exist at temperatures relevant for atmospheric modeling (i.e., $T < 298$ K).

In this paper we report the results of a flash photolysis–resonance fluorescence kinetics study of reactions 1–4 over the temperature range 244–367 K. The data are compared with previously reported results, and their mechanistic and atmospheric implications are discussed.

(1) J. N. Galloway and D. M. Whelpdale, *Atmos. Environ.*, **14**, 409 (1980).
(2) C. F. Cullis and M. M. Hirschler, *Atmos. Environ.*, **14**, 1263 (1980).
(3) L. Granat, H. Rodhe, and R. O. Hallberg, in "Nitrogen, Phosphorous, and Sulphur—Global Cycles", B. M. Svensson and R. Söderlund, Eds., SCOPE Report 7, Swedish Natural Science Research Council, Stockholm, 1976, pp 89–134.
(4) H. Rodhe and I. Isaksen, *J. Geophys. Res.*, **85**, 7401 (1980).
(5) T. E. Graedel, *Rev. Geophys. Space Phys.*, **15**, 421 (1977).
(6) F. Stuhl, *Ber. Bunsenges. Phys. Chem.*, **78**, 231 (1974).
(7) R. A. Perry, R. Atkinson, and J. N. Pitts, Jr., *J. Chem. Phys.*, **64**, 3237 (1976).
(8) J. V. Michael, D. F. Nava, W. D. Brobst, R. P. Borkowski, and L. J. Stief, *J. Phys. Chem.*, submitted.
(9) A. A. Westenberg and N. deHaas, *J. Chem. Phys.*, **59**, 6885 (1973).
(10) M. T. Leu and R. H. Smith, *J. Phys. Chem.*, submitted.
(11) R. Atkinson, R. A. Perry, and J. N. Pitts, Jr., *J. Chem. Phys.*, **66**, 1578 (1977).
(12) R. Atkinson, R. A. Perry, and J. N. Pitts, Jr., *Chem. Phys. Lett.*, **54**, 14 (1978).
(13) M. J. Kurylo, *Chem. Phys. Lett.*, **58**, 233 (1978).
(14) R. A. Cox and D. Sheppard, *Nature (London)*, **284**, 330 (1980).

TABLE I: Monitoring Wavelengths and Absorption Cross Sections Employed to Measure the Fraction of Reactant in the Reactant/Ar Storage Bulbs

reactant	monitoring wavelength, nm	absorption cross section, 10^{-19} cm^2
H_2S	185.0 (Hg lamp)	38.2
CH_3SH	228.8 (Cd lamp)	6.70
CH_3SCH_3	228.8 (Cd lamp)	11.6
CH_3SSCH_3	185.0 (Hg lamp)	159

Experimental Section

The apparatus used in this study has been described previously.[15] Hence, only a brief review of its operation is given below.

A jacketed Pyrex reaction cell with an internal volume of ~150 cm^3 was used in all experiments. The cell was maintained at a known constant temperature by circulating an ethylene glycol–water mixture from a thermostated bath through the outer jacket. OH radicals were produced by flash photolysis of H_2O at wavelengths between the onset of absorption at 185 nm and the Suprasil cutoff at ~165 nm. An OH resonance lamp situated perpendicular to the flash lamp excited fluorescence in the 0–0 band of the $A^2\Sigma^+$–$X^2\pi$ system. Fluorescence was detected perpendicular to both the flash lamp and the resonance lamp by a photomultiplier fitted with an interference filter (3095-Å peak transmission, 100-Å fwhm). Signals were obtained by photon counting and then fed into a signal averager operating in the multichannel scaling mode. For each decay rate measured, sufficient flashes were averaged to obtain a well-defined temporal profile over at least two and usually three $1/e$ times. The flash duration was ~50 μs while measured OH lifetimes ranged from 0.95 to 43 ms.

In order to avoid accumulation of reaction or photolysis products, all experiments were carried out under "slow flow" conditions. Reactant (i.e., H_2S, CH_3SH, CH_3SCH_3, or CH_3SSCH_3) was flowed from a 12-L bulb containing a dilute reactant/Ar mixture. An H_2O/Ar mixture was generated by bubbling Ar through high-purity water at room temperature and a pressure of 800 torr. The reactant mixture, the H_2O mixture, and additional diluent gas were premixed before entering the reaction cell. Concentrations of each component in the reaction mixture were determined from measurements of the appropriate mass flow rates and the total pressure.

The fraction of reactant in the reactant/Ar mixture was checked frequently by simultaneous measurement of the total pressure (of the mixture) and UV absorption by the reactant. Atomic line sources were used in conjunction with an 82-cm absorption cell and a band-pass filter–photomultiplier detector to carry out these measurements. The monitoring wavelength and the absorption cross section employed to measure each reactant are summarized in Table I. The needed absorption cross sections were measured during the course of the investigation and found to agree well with published values[16] in all cases.

The gases used in this study had the following stated purities: Ar ≥ 99.9995%, H_2S ≥ 99.5%, and CH_3SH ≥ 99.5%. H_2S and CH_3SH were degassed repeatedly at 77 K before use. Ar was used as supplied. CH_3SCH_3 and CH_3SSCH_3 were obtained in liquid form from Eastman Organic Chemicals; sample purities are typically in the range 98–99%.[17] The liquid samples were transferred into Pyrex tubes fitted with high-vacuum stopcocks, degassed several times at 77 K, and then stored under vacuum on a gas handling system. The tube containing CH_3SSCH_3 was blackened to prevent absorption of room light. The samples were subjected to additional degassing immediately before use. UV spectra of vapor-phase samples of CH_3SH, CH_3SCH_3, and CH_3SSCH_3 were run on a Cary 17 spectrophotometer. The spectra agreed very well in both wavelength dependence and absorption coefficient with published spectra;[16] 100 torr of CH_3SCH_3 sample gave no measurable absorption at 280 nm, indicating less than 0.1% CH_3SSCH_3 contamination.

Results

To measure the desired bimolecular rate constants, it is desirable to establish experimental conditions where the OH temporal profile is governed by the following processes:

$$H_2O \xrightarrow{h\nu} H + OH \qquad (5)$$

$$OH + R_i \xrightarrow{k_i} \text{products} \qquad i = 1\text{–}4,\ R_i = \text{reactant} \qquad (6)$$

$$OH \xrightarrow{k_d} \text{loss by diffusion from field of view of detector and reaction with background impurities} \qquad (7)$$

Then, if [R] ≫ [OH] (pseudo-first-order conditions), simple first-order kinetics will be obeyed:

$$\ln\{[OH]_0/[OH]_t\} = (k_i[R] + k_d)t \equiv k't \qquad (I)$$

The bimolecular rate constant, k_i, is determined from the slope of a k' vs. [R] plot. Observation of OH temporal profiles which are exponential (i.e., obey eq I), a linear dependence of k' on [R], and invariance of k_i to variations in experimental parameters such as the flash intensity and the water concentration serve as proof that reactions 5–7 are, indeed, the only processes which affect the OH time history and, therefore, validate the measurement of k_i. (The presence of reactive impurities in the reactant sample will, of course, not be detected by such a kinetic analysis.)

Under typical operating conditions (flash energy ≈ 60 J, $[H_2O]$ = 0.15 torr) 5×10^{10}–10×10^{10} OH radicals cm^{-3} are produced by the photoflash.[15] Therefore, we did not expect reactions of OH with itself or with reaction products to contribute to the observed temporal profile. This expectation was confirmed experimentally by showing that k_i was not affected by a factor of 3 reduction in $[H_2O]$ at constant flash intensity.

To investigate the possibility that reactive free radicals generated by photodissociation of reactants could contribute to the observed OH temporal behavior, we carried out experiments where the flash intensity was varied by a factor of 3 or more at constant $[H_2O]$. Only in the case of reaction 1 was evidence observed for secondary chemistry complications. Measurements at flash energies of ~120 J gave k_1 values which were 10–15% higher than those measured at lower flash energies. No dependence of k_1 on flash energy was observed in the 20–72-J range, so the high flash intensity data were ignored in the determination of k_1.

Because reaction 4 was found to proceed at a near gas kinetic rate, CH_3SSCH_3 concentrations as low as 1×10^{12} molecules cm^{-3} were used in some experiments. To ensure the existence of pseudo-first-order conditions, therefore, all measurements of k_4 employed $[H_2O]$ = 0.06 torr. Under these experimental conditions, all OH decays were found to be exponential for more than two $1/e$ times (Figure 1).

(15) P. H. Wine, N. M. Kreutter, and A. R. Ravishankara, *J. Phys. Chem.*, 83, 3191 (1979), and references therein.

(16) J. G. Calvert and J. N. Pitts, Jr., "Photochemistry", Wiley, New York, 1966.

(17) R. Hawryluk, Eastman Organic Chemicals, private communication.

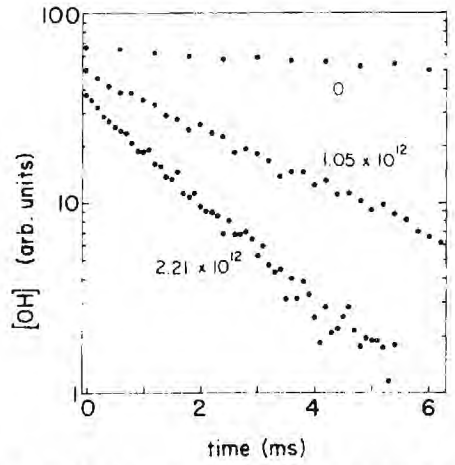


Figure 1. Typical OH temporal profiles observed following flash photolysis of H_2O/Ar/reactant mixtures. Reactant: CH_3SSCH_3. Experimental conditions: $T = 249$ K; $P = 50$ torr; $P_{H_2O} = 0.06$ torr; flash energy = 61 J; CH_3SSCH_3 concentrations in units of molecules cm^{-3} are given in the figure.

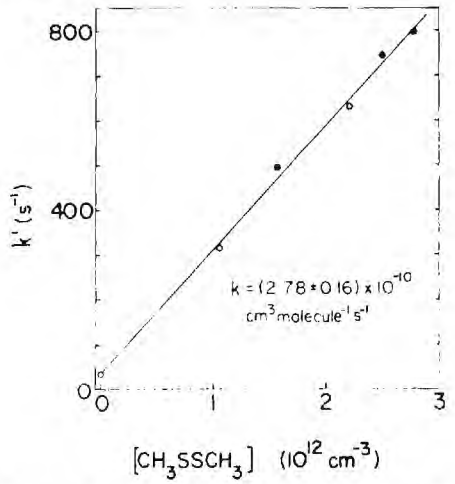


Figure 2. Typical k' vs. [R] data. Reactant: CH_3SSCH_3. Experimental conditions: $T = 249$ K; $P = 50$ torr; $P_{H_2O} = 0.06$ torr; flash energy = 61 J. The open circles represent the three pseudo-first-order rate constants determined from the data shown in Figure 1. The line is obtained from an unweighted linear least-squares analysis.

Furthermore, k_4 was found to be independent of a factor of 3 (39–115 J) variation in flash energy. Hence, we are confident that none of the results for reaction 4 requires correction for deviation from first-order kinetics.

A total of 319 experiments (experiment ≡ determination of one pseudo-first-order rate constant) were carried out. For each reaction studied varying conditions of pressure, temperature, water concentration, and flash intensity were employed. Typical OH temporal profiles are shown in Figure 1. A typical plot of k' vs. [R] is shown in Figure 2. Exponential OH decays and linear dependences of k' on [R] were observed in all cases. None of the rate constants was found to be pressure dependent over the ranges investigated (40–120 torr of Ar for H_2S and CH_3SH, 50–200 torr of Ar for CH_3SCH_3 and CH_3SSCH_3). The experimental results are summarized in Table II. Errors quoted for individual k_i determinations are 2σ and refer only to the precision of the k' vs. [R] data. Where two or more k_i's were averaged to obtain a rate constant, the overall precision is conservatively chosen to bracket all individual k_i's and their 2σ uncertainties. In the three cases where only one $k_i(T)$ was determined, the uncertainty is set at ±15%, which is a little larger than the typical uncertainty observed when several determinations were averaged. The

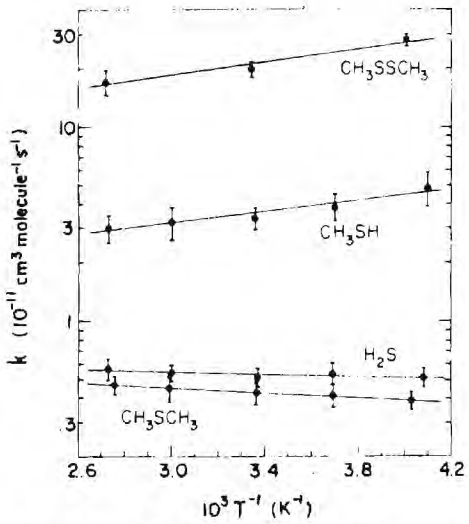


Figure 3. Arrhenius plots of the experimental results. Errors are chosen so as to bracket all measured $k_i \pm 2\sigma$ values.

absolute accuracy of the results is limited by both precision and uncertainties in the determination of the reactant concentration. We estimate the absolute accuracy of $k_i(T)$ to be better than 20%.

The data for each of the four reactions investigated are adequately described in Arrhenius form (i.e., a linear ln k vs. T^{-1} dependence). Unweighted linear least-squares analyses give the following Arrhenius expressions (units are cm^3 molecule^{-1} s^{-1}):

$$k_1 = (6.4 \pm 1.3) \times 10^{-12} \exp[(-55 \pm 58)/T]$$

$$k_2 = (1.15 \pm 0.39) \times 10^{-11} \exp[(+338 \pm 100)T]$$

$$k_3 = (6.8 \pm 1.1) \times 10^{-12} \exp[(-138 \pm 46)/T]$$

$$k_4 = (5.9 \pm 3.3) \times 10^{-11} \exp[(+380 \pm 160)T]$$

The errors in the above expressions are 2σ and represent precision only. The experimental rate constants and best-fit Arrhenius lines are plotted in Figure 3. The temperature dependence observed for k_1 was so weak that a temperature-independent rate constant of $(5.35 \pm 0.40) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} would also be an adequate representation of the data.

Discussion

Kinetic data obtained in this investigation are compared with results from other laboratories in Figures 4 and 5.

With the exception of the discharge flow–ESR study of Westenberg and deHaas,[9] there is general agreement that reaction 1 has little or no temperature dependence over the range of temperatures relevant to the atmosphere. In a discharge flow–resonance fluorescence study Leu and Smith[10] observed an unusual temperature dependence with $k_1(T)$ actually going through a minimum when $T \approx 280$ K. Michael et al.,[8] using the flash photolysis–resonance fluorescence technique, report rate constants at three temperatures (228, 298, and 437 K) which support the findings of Leu and Smith. However, these authors point out that a temperature-independent k_1 would also be an adequate representation of their data. Our results and those of Perry et al. are not sufficiently precise and do not cover a broad enough temperature range to either support of refute the temperature dependence observed by Leu and Smith. It is interesting to note that the results of all temperature-dependent studies "converge" in the tropospheric temperature regime such that, for $230 < T < 300$ K, a value $k_1 = (4.6 \pm 1.0) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} is

TABLE II: Rate-Constant Data for the Reactions of OH with H_2S, CH_3SH, CH_3SCH_3, and CH_3SSCH_3

reaction	T, K	P, torr	P_{H_2O}, torr	flash energy, J	linear flow rate,[a] cm s^{-1}	no. of experiments	$10^{12}(k_i \pm 2\sigma)$, cm^3 molecule^{-1} s^{-1}	av $10^{12}k_i$,[b] cm^3 molecule^{-1} s^{-1}
OH + H_2S	245	40	0.12	20	2.1	8	5.18 ± 0.58	
		40	0.12	120	2.1	6	5.97 ± 0.43[c]	
		40	0.10	39	2.1	5	5.14 ± 0.23	5.16 ± 0.56
	271	95	0.19	61	2.0	5	5.22 ± 0.17	
		40	0.15	72	2.1	7	5.49 ± 0.57	
		40	0.15	31	2.1	5	5.46 ± 0.25	5.39 ± 0.67
	297	44	0.19	61	2.3	6	5.06 ± 0.30	
		40	0.05	61	2.1	6	5.33 ± 0.26	
		40	0.15	31	2.1	8	5.10 ± 0.36	
		40	0.15	39	2.1	7	5.03 ± 0.47	5.13 ± 0.57
	333	40	0.16	61	2.2	5	5.53 ± 0.36	
		40	0.15	31	2.1	8	5.30 ± 0.26	5.41 ± 0.48
	366	40	0.15	115	2.1	7	6.24 ± 0.73[c]	
		40	0.15	39	2.1	7	5.76 ± 0.58	
		120	0.14	72	3.1	4	5.51 ± 0.45	
		120	0.15	72	1.0	6	5.76 ± 0.40	
		40	0.15	20	2.1	7	5.63 ± 0.56	5.66 ± 0.68
OH + CH_3SH	244	40	0.13	65	2.1	6	53.7 ± 4.4	
		40	0.15	65	2.1	6	49.2 ± 1.8	
		120	0.14	65	1.0	5	49.5 ± 1.6	
		120	0.13	65	3.1	5	40.9 ± 1.6	48.3 ± 9.8
	270	40	0.15	72	2.1	9	38.4 ± 2.4	38.4 ± 5.8
	298	40	0.15	39	2.1	5	33.8 ± 3.0	
		40	0.15	115	2.1	6	34.8 ± 1.8	
		40	0.05	72	2.1	4	32.4 ± 2.8	
		40	0.13	65	2.1	6	33.9 ± 1.5	33.7 ± 4.1
	333	40	0.15	72	2.1	7	29.7 ± 1.6	
		40	0.15	72	2.1	5	34.6 ± 3.8	32.2 ± 6.2
	366	40	0.15	39	2.1	5	29.5 ± 4.5	
		40	0.14	65	2.1	6	28.4 ± 0.9	
		40	0.15	115	2.1	6	32.3 ± 1.7	
		120	0.15	72	1.0	7	29.2 ± 3.6	
		120	0.15	72	3.0	6	29.2 ± 1.0	29.7 ± 4.7
OH + CH_3SCH_3	248	50	0.11	31	1.6	6	3.99 ± 0.23	
		50	0.13	125	1.4	4	3.78 ± 0.29	3.89 ± 0.38
	271	50	0.12	31	1.6	5	4.31 ± 0.12	
		50	0.13	125	1.6	6	4.33 ± 0.37	
		100	0.11	72	1.5	6	3.82 ± 0.15	4.15 ± 0.55
	298	50	0.15	72	1.5	6	4.37 ± 0.44	
		50	0.14	72	1.5	7	4.14 ± 0.24	
		50	0.05	72	1.6	6	4.23 ± 0.53	
		50	0.15	20	1.5	6	4.21 ± 0.30	
		50	0.15	72	1.6	4	4.33 ± 0.43	4.26 ± 0.56
	334	50	0.15	31, 125	1.5	7	4.50 ± 0.30	4.50 ± 0.68
	363	50	0.14	72	1.6	5	4.50 ± 0.34	
		200	0.15	72	1.5	5	4.80 ± 0.19	
		100	0.13	72	1.6	6	4.70 ± 0.38	4.67 ± 0.51
OH + CH_3SSCH_3	249	50	0.06	61	3.0	5	282 ± 15	
		50	0.06	61	3.0	6	278 ± 16	280 ± 18
	298	50	0.06	39	3.0	4	192 ± 10	
		50	0.06	115	3.0	3	203 ± 7	
		200	0.06	61	2.9	4	191 ± 11	
		50	0.06	61	3.0	4	204 ± 3	198 ± 18
	367	50	0.06	61	3.0	5	171 ± 10	171 ± 25

[a] Linear flow rate ≡ measured mass flow rate (units of standard cm^3 s^{-1}) × 760/P(torr) divided by the cross-sectional area of the reactor. [b] Uncertainties are chosen to bracket all measured rate constants including their 2σ errors. Where only a single k_i was determined, the uncertainty is assumed to be ±15% in keeping with the uncertainties observed in the other cases. [c] Due to suspected secondary chemistry complications, these data were not included in the determination of the average value of $k_i(T)$.

onsistent with all available data except the 298 K result f Stuhl.[6] Thus, it appears that k_1 is known with reasonble accuracy for the purpose of atmospheric modeling. owever, the unusual temperature dependence observed y Leu and Smith suggests that the mechanism may be mewhat more complex than a simple H atom abstraction. Our study of reaction 2 is in excellent agreement with n earlier flash photolysis–resonance fluorescence study y Atkinson et al.[11] Cox and Sheppard,[14] using competitive kinetics techniques, report a value for k_2 at 298 K about a factor of 3 larger than what is obtained from either direct measurement. These authors suggest that reaction 2 may be faster under their conditions (1 atm of air) than under the reduced pressure conditions employed in the flash photolysis studies. We find k_2 to be independent of pressure over the range 40–120 torr of Ar. This finding does not, however, preclude the possibility of a small termolecular channel which becomes much more important

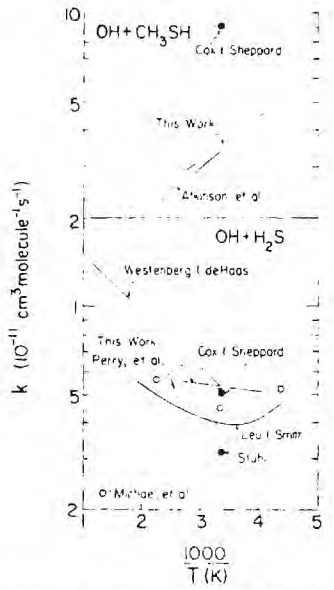


Figure 4. Comparison of our results for reactions of OH with H_2S and CH_3SH with those of other investigators.

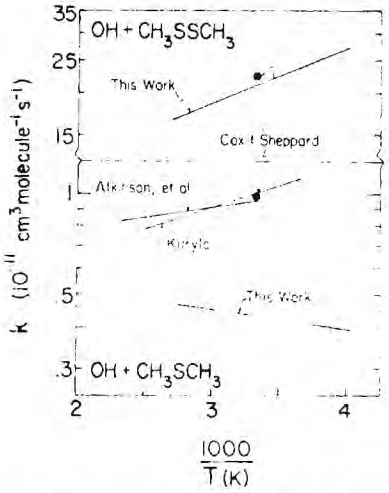


Figure 5. Comparison of our results for the reactions of OH with CH_3SCH_3 and CH_3SSCH_3 with those of other investigators. The line representing Kurylo's data was generated by taking his $k_3(T)$ values and carrying out an unweighted linear least-squares analysis of ln k_3 vs. T^{-1}.

at 1-atm pressure and in the presence of more efficient third bodies. It is also possible that a weakly bound $CH_3SH\cdots OH$ complex, if formed, could react with O_2 before decomposing. A similar mechanism has been proposed to account for the observed pressure-dependent rate constant for the reaction of OH with CO.[18] Clearly, a direct measurement of k_2 under conditions of atmospheric pressure and gas composition would be desirable.

The most interesting result obtained in this investigation is our determination that k_3 is more than a factor of 2 lower than the value obtained (with excellent agreement) in three other laboratories.[12-14] Furthermore, we observe a small positive temperature dependence whereas two previous investigations both report a small negative temperature dependence.[12,13] One major difference between our study and the two previous flash photolysis studies[12,13] is the spectral distribution of the photoflash. We employed Suprasil optics which transmit only at $\lambda > 165$ nm while both earlier studies employed lithium fluoride optics which transmit at $\lambda > 105$ nm. The potential for secondary chemistry involving CH_3SCH_3 photofragments was, therefore, greater in the earlier studies than in our study. Both previous studies, however, report k_3 to be independent of flash intensity, a fact which argues against secondary chemistry involving reactant photofragments being the reason for their higher k_3 values. Another potential explanation for the discrepancies between our results and the two previous flash photolysis studies is the possibility that reactive impurities were present in the CH_3SCH_3 samples used in the earlier investigations. The major impurities in CH_3SCH_3 samples are CH_3SH and CH_3SSCH_3,[17] but, upon exposure to air, CH_3SH is oxidized to CH_3SSCH_3.[19] Our values for k_3 and k_4 predict that reaction of OH with a mixture containing 98% CH_3SCH_3 and 2% CH_3SSCH_3 should give almost exactly the magnitude and temperature dependence reported for k_3 in the two previous flash photolysis studies. It is worth noting, however, that our own experience indicates that handling CH_3SCH_3 is not particularly difficult. The competitive kinetics study of Cox and Sheppard[14] directly monitoried the disappearance of CH_3SCH_3 during continuous OH production by near-UV photolysis of HONO. Hence, this study could not have been affected by either of the potential sources of error discussed above. However, as in any indirect study, interpretation of the results requires a complete understanding of system chemistry. If CH_3SCH_3 was consumed by processes other than reaction 3, overestimation of k_3 would result.

The values for $k_3(T)$ reported in this investigation are very similar in both magnitude and T dependence to those reported for the reaction of OH with CH_3OCH_3 by Perry et al.[20] These authors calculated a rate constant per C–H bond of 5.8×10^{-13} cm^3 molecule^{-1} s^{-1} at 299 K, in excellent agreement with the results of Greiner[21] that, for OH attack on secondary C–H bonds in alkanes (which are similar in strength to the C–H bonds in CH_3OCH_3), the rate constant per bond is $\sim 5.6 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K. From this comparison it was concluded that OH attack on CH_3OCH_3 proceeds with the same mechanism as OH attack on secondary alkanes, namely, H atom abstraction. For CH_3SCH_3, we obtain a rate constant per C–H bond of 7.1×10^{-13} cm^3 molecule^{-1} s^{-1} at 298 K, which strongly suggests that the dominant reaction path is H atom abstraction. The slightly larger rate constant per bond for CH_3SCH_3 vs. CH_3OCH_3 probably reflects a weaker C–H bond in the former although a small but significant addition channel cannot be eliminated as a possibility.

Our results for k_4 are in excellent agreement with the 298 K measurement of Cox and Sheppard. Since reaction 4 is $\sim$50 times faster than reaction 3, it must be that OH reaction with CH_3SSCH_3 proceeds primarily by attack at the weak S–S bond. The observed negative temperature dependence provides evidence that an adduct is initially formed, although rapid decomposition to $CH_3S + CH_3SOH$ is quite likely.

Implications for Atmospheric Chemistry

Our results confirm that OH radicals react rapidly with all hydrogen-containing reduced sulfur compounds of atmospheric importance. We can obtain maximum tropospheric residence times, τ_i, from the following relationship:

$$\tau_i^{-1} = k_i[\mathrm{OH}] \qquad \text{(II)}$$

(18) H. W. Biermann, C. Zetsch, and F. Stuhl, *Ber. Bunsenges. Phys. Chem.*, **82**, 633 (1978).

(19) J. D. Roberts and M. C. Caserio, "Basic Principles of Organic Chemistry", W. A. Benjamin, New York, 1965.

(20) R. A. Perry, R. Atkinson, and J. N. Pitts, Jr., *J. Chem. Phys.*, **67**, 611 (1977).

(21) N. R. Greiner, *J. Chem. Phys.*, **53**, 1070 (1970).

where [OH] is an average value over the appropriate time interval. OH levels are highly variable, depending upon the local concentrations of O_3, H_2O, CO, CH_4, and NO_x, and also the solar UV flux. Recent measurements[22] suggest that the annually and diurnally averaged OH concentration in the tropical marine boundary layer is 2×10^6 molecules cm^{-3}. Using this value as a rough estimate for the average [OH] encountered by reduced sulfur compounds in the lower troposphere, we obtain the following lifetimes from our results for k_i at 298 K: τ_{H_2S} = 27 h, τ_{CH_3SH} = 4.1 h, $\tau_{CH_3SCH_3}$ = 33 h, and τ_{CH_3SSCH} = 42 min. Midday OH levels are a factor of ~3 larger than the diurnally averaged values, so the residence times of the short-lived species CH_3SH and CH_3SSCH_3 will be a factor of 3 shorter at midday than the diurnally averaged estimates suggest.

One current problem in atmospheric sulfur chemistry centers around determining the origin of the relatively high (~100 pptv), uniformly distributed SO_2 levels recently measured in the upper troposphere.[23] Because of their short lifetimes, none of the compounds studied in this investigation can be transported from their ground (or ocean) sources to the upper troposphere. Therefore, only if there exist airborne sources can hydrogen-containing reduced sulfur compounds be precursors for free tropospheric SO_2 (SO_2 itself is removed by OH and heterogeneous processes with a lifetime of ~10 days; hence, the uniformly distributed SO_2 levels imply the existence of a nearly uniformly distributed precursor).

Whereas H_2S is generally thought to enter the atmosphere primarily from localized sources such as swamps and marshes, recent measurements indicate that the ocean is the primary source of CH_3SCH_3 with the diurnally averaged concentration over the ocean being 58 pptv.[24] Model calculations[25] using the combined results of Atkinson et al.[12] and Kurylo[13] for $k_3(T)$, and assuming unit conversion of CH_3SCH_3 to SO_2, demonstrate that oxidation of CH_3SCH_3 can produce ~100 pptv SO_2 in the marine boundary layer—ca. twice the measured concentration.[23] Our values for $k_3(T)$ would reduce the calculated SO_2 source by a factor of ~2.3.

Neither CH_3SH nor CH_3SSCH_3 has been observed in the atmosphere except in the vicinity of large anthropogenic or biogenic sources. However, the very rapid rates at which these species react with OH suggest that undectectably low steady-state concentrations could be present even though reasonably large-scale sources exist. This is particularly true of CH_3SSCH_3. A CH_3SSCH_3 source equal to that for CH_3SCH_3 would imply an atmospheric CH_3SSCH_3 concentration of ~1 pptv, a level which may not be measurable with presently available techniques.

Acknowledgment. We thank D. H. Semmes and R. C. Shah for assisting with some of the experiments and Professor W. L. Chameides for helpful discussions concerning the atmospheric implications of our results. This work was supported by the National Science Foundation through grant no. ATM-80-19040.

(22) D. D. Davis, W. L. Chameides, D. Philen, W. Heaps, A. R. Ravishankara, and M. Rodgers, *J. Geophys. Res.*, submitted.
(23) P. J. Maroulis, A. L. Torres, A. B. Goldberg, and A. R. Bandy, *J. Geophys. Res.*, **85**, 7345 (1980).
(24) P. J. Maroulis and A. R. Bandy, *Science*, **196**, 647 (1977).
(25) J. A. Logan, M. B. McElroy, S. C. Wofsy, and M. J. Prather, *Nature (London)*, **281**, 185 (1979).

APPENDIX II

Reprint of the Paper

POTENTIAL ROLE OF CS_2 PHOTOOXIDATION IN TROPOSPHERIC SULFUR CHEMISTRY

GEOPHYSICAL RESEARCH LETTERS, VOL. 8, NO. 5, PAGES 543-546, MAY 1981

POTENTIAL ROLE OF CS_2 PHOTOOXIDATION IN TROPOSPHERIC SULFUR CHEMISTRY

P. H. Wine,[1] W. L. Chameides,[2] and A. R. Ravishankara[a]

Georgia Institute of Technology
Atlanta, GA 30332

Abstract. Electronically excited CS_2 (CS_2*) is found to be rapidly produced in the troposphere from the absorption of solar photons by ground state CS_2 molecules. The chemical reaction of CS_2* with O_2 can, if the CS + SOO yield is greater than 0.01, remove tropospheric CS_2 on a time scale of one or two weeks. Assuming a ground level background CS_2 concentration of 20 pptv and an OCS lifetime of 1 year, calculations indicate that this photooxidation mechanism can be a major source of tropospheric OCS but only a minor source of SO_2.

Introduction

Oxidation of carbon disulfide (CS_2) may lead to the production of carbonyl sulfide (OCS), the predominant sulfur containing compound in the troposphere [Hanst, et al, 1975; Torres, et al, 1980]. OCS is relatively inert in the troposphere and hence can be transported to the stratosphere where it photodissociates rapidly. Oxidation of the resulting sulfur atoms is believed to contribute significantly to the formation of stratospheric sulphate aerosol [Crutzen, 1976], thus affecting the earth's radiation budget and climate. For this reason, there is considerable current interest in identifying the sources of atmospheric OCS.

The potential importance of CS_2 oxidation as a source for OCS (and also SO_2) has been discussed in several recent papers [Sze and Ko, 1979 a, b; Logan, et al, 1979; Turco, et al, 1980]. In all cases, however, the oxidation mechanism was assumed to be initiated by hydroxyl radical attack on CS_2:

$$OH + CS_2 \longrightarrow SH + OCS \qquad (1)$$

$k_1 = 1.9 \times 10^{-13}$ cm^{3}molecule^{-1}s^{-1} [Kurylo, 1978].

Furthermore, background CS_2 levels of $\geq$ 70 pptv [Sandalls and Penkett, 1977] were assumed in all cases. It has recently been shown that k_1 (298K) is less than 1.5×10^{-15} cm^3 molecule^{-1}s^{-1} [Wine, et al, 1980; Iyer and Rowland, 1980]; hence, Reaction (1) can no longer be considered a viable sink for tropospheric CS_2. Furthermore, recent measurements indicate that CS_2 mixing ratios on the order of 100 pptv are found only in industrialized areas and that background CS_2 levels are 30 pptv or less at ground level [Maroulis and Bandy, 1980] and less than 3 pptv in the free troposphere [Shalaby, et al, 1980]. The large temporal variability in CS_2 found by Maroulis and Bandy [1980] and the sharp CS_2 vertical gradient observed by Shalaby, et al [1980] suggest that the tropospheric lifetime of CS_2 is short — a week or two at most. Hence, an efficient CS_2 removal process other than Reaction (1) must exist.

One possible CS_2 destruction mechanism which warrants consideration is photooxidation:

$$CS_2 \xrightarrow[\lambda > 280\ nm]{h\upsilon} CS_2^* \qquad (2)$$

$$CS_2^* + O_2 \xrightarrow{k_3} \begin{cases} \xrightarrow{M} CS + SOO & (3a) \\ \longrightarrow CS_2 + O_2. & (3b) \end{cases}$$

Evidence for Reaction (3a) was observed in flash photolysis experiments by deSorgo, et al [1965]. Later, Wood and Heicklen [1971], using cw photolysis (313 nm) — end product analysis techniques, deduced that $k_{3a}/k_{3b} \sim .05$. Reaction (3a) was suggested as a possible tropospheric CS_2 sink by Sandalls and Penkett [1977] and by Sze and Ko [1979b]. However, because Reaction (1) was thought to adequately account for CS_2 removal and because experimental data concerning the photooxidation process was sparse, no quantitative evaluation of the potential importance of Reaction (3a) has been carried out. In this communication we present the results of absorption cross section measurements and model calculations which suggest that photooxidation may be an important tropospheric sink for CS_2 and that oxidation of CS, a product of Reaction (3a), may be an important source of OCS.

CS_2 Photoexcitation Rate

CS_2 absorption cross sections in the 280-360 nm wavelength region have not previously been measured with sufficient accuracy to allow calculation of an accurate tropospheric photoexcitation rate. Hence, we have measured the needed cross sections. Reagent grade CS_2 was vacuum distilled and degased several times before use. Absorption spectra were recorded on a Cary 14 spectrophotometer using a 10 cm brass cell equipped with quartz windows. The spectral resolution was $\sim$ 0.4 nm. Pure CS_2 was used in most runs since it was found that addition of one atmosphere of air did not result in measurable broadening of the spectrum. A majority of the data was obtained using CS_2 pressures of 35 Torr (290-347.5 nm) and 290 Torr (280-297.5 nm and 335-360 nm). Additional pressure dependent data were obtained at a few wavelengths to firmly establish that Beer's law was obeyed over a wide range of [CS_2]. Cross sections were computed at 0.25 nm intervals. Results for T = 298 K are plotted in Figure 1.

Diurnally averaged photoexcitation rates, j_{av}, for 30°N latitude at equinox were calculated using a two-stream algorithm to simulate the transfer of solar radiation through an absorbing and multiply scattering atmosphere; optical data were taken from Arveson, et al [1969] and Hudson and Reed [1979]. Very low resolution differential photoexcitation rates (altitude = 0 km) are plotted as a function of wavelength in Figure 1. The computed j_{av} values increase monotonically as a function of altitude from 4.5×10^{-5} s^{-1} at 0 km to 8.9×10^{-5} s^{-1} at 10 km. Thus, the lifetime of CS_2 toward conversion to CS_2* is a few hours. It should be noted that in spite of the short photoexcitation lifetime, the use of diurnally averaged solar flux data is a reasonable approximation because most CS_2* is apparently deactivated by physical quenching [Wood and Heicklen, 1971]. Thus, the lifetime of CS_2 toward photodestruction is probably longer than 1 day.

Many of the strongest features of the CS_2 absorption spectrum are known to result from "hot" bands (i.e., absorption from vibrationally excited CS_2) [Jungen, et al, 1973]. Hence, the possibility exists that j_{av} could be strongly temperature dependent. To explore this possibility absorption spectra were recorded as a function of temperature over the range 250K < T < 325K. Only small differences (on the order of 10%) in the integrated photoexcitation rates were obtained. These differences were ignored in the calculations discussed below.

1. Molecular Sciences Group, Engineering Experiment Station
2. School of Geophysical Sciences

Paper number 1L0725.
0094-8276/81/001L-0725$01.00

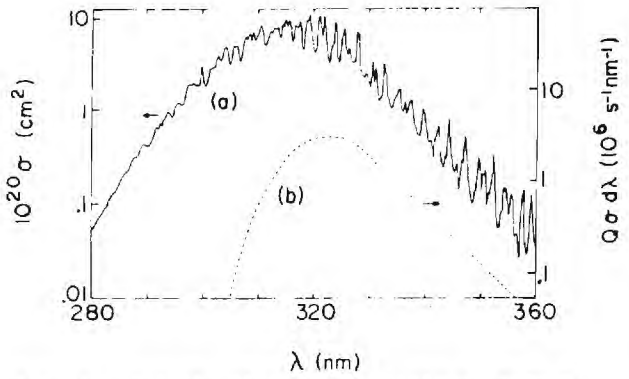


Fig. 1. (a) CS_2 absorption spectrum, T=298K. (b) Wavelength dependence of the product of the solar flux and the absorption cross section.

Photochemical Mechanism

In the absence of collisions, the fate of CS_2* is fluorescence [Heicklen, 1963].

$$CS_2^* \longrightarrow CS_2 + h\nu. \qquad (-2)$$

Excitation at 337 nm produces two radiating states with lifetimes of 2.9 μsec and 17μsec [Brus, 1971; Silvers and McKeever, 1976], while excitation at 320 nm produces a single radiating state with a lifetime of ~ 15 μsec [Lambert and Kimbell, 1973]. Fluorescence quenching by N_2 and O_2 has been studied by Brus [1971] for 337 nm excitation and by Lambert and Kimbell [1973] for 320 nm excitation. The 2.9 μsec state is quenched at a gas kinetic rate by both N_2 and O_2 while the quenching rates measured for the longer lived states are in the range 2-5 × 10^{-11} cm^{3}molecule^{-1}s^{-1}.

The lifetimes and quenching rates discussed above suggest that, under tropospheric conditions, fluorescence is a negligible CS_2* removal process as are reactions with atmospheric trace constituents such as O_3. The important processes are Reactions (3a), (3b) and the additional quenching reactions

$$CS_2^* + N_2 \longrightarrow CS_2 + N_2 \qquad (4)$$

$$CS_2^* + H_2O \longrightarrow CS_2 + H_2O. \qquad (5)$$

k_5 is not known but is probably near gas kinetic. If the products of Reactions (3a), (3b), (4), and (5) are formed directly from CS_2* deactivation (an assumption which has not been verified experimentally) then Wood and Heicklen's results that $k_{3a}/k_{3b} \sim .05$ would, in conjunction with the fluorescence quenching results, imply a quantum yield for CS + SOO formation under tropospheric conditions of .01 ~ .015.

The fate of CS produced from Reaction 3a is probably reaction with O_2:

$$CS + O_2 \xrightarrow{k_6} \begin{cases} \longrightarrow OCS + O & (6a) \\ \longrightarrow CO + SO & (6b) \end{cases}$$

k_6 (293K) = 4.5 × 10^{-19} cm^{3}molecule^{-1}s^{-1} [Richardson, 1975]. The reaction

$$CS + O_3 \xrightarrow{k_7} \begin{cases} \longrightarrow OCS + O_2 & (7a) \\ \longrightarrow SO + CO_2 & (7b) \\ \longrightarrow CO + SO_2 & (7c) \end{cases}$$

would also be important if $k_7 > 1 \times 10^{-12}$ cm^{3}molecule^{-1}s^{-1} or if k_7 is significantly slower than Richardson's value. Heterogeneous removal of CS is probably much too slow to be important.

The branching ratio k_{6a}/k_{6b} is in question. Richardson [1975] found Reaction (6a) to be the dominant channel, $k_{6a} > 9\ k_{6b}$, while Wood and Heicklen [1971] found $k_{6a} \approx 1.2\ k_{6b}$. Olszyna and Heicklen [1970] report indirect evidence that OCS, CO_2, and CO are formed from Reaction (7) in the ratio 0.555:0.097:0.348. SO formed in Reactions (6b) and (7b) is rapidly oxidized to SO_2:

$$SO + O_2 \longrightarrow SO_2 + O \qquad (8)$$

k_8 (298K) = 9 × 10^{-18} cm^{3}molecule^{-1}s^{-1} [Baulch, et al, 1980].

Clearly, the relative yields of OCS and SO_2 from CS_2 photooxidation depend critically on the branching ratio for Reaction (6) and, if it is fast enough to be competitive, Reaction (7) as well.

Using the above photochemical scheme and including reaction with OH as an additional loss mechanism for OCS and formation mechanism for SO_2

$$OH + OCS \xrightarrow{k_9} \text{products} \longrightarrow SO_2 \qquad (9)$$

k_9 = 8.8 × 10^{-15} cm^{3}molecule^{-1}s^{-1} [Ravishankara, et al, 1980], we obtain the following rate equations for CS_2 removal and OCS, SO_2 formation:

$$\text{CS}_2 \text{ loss rate} = \left(\frac{k_{3a}[O_2]}{k_3[O_2] + k_4[N_2] + k_5[H_2O]} \right) j_{es}[CS_2] \equiv \Phi_{CS}\, j_{es}[CS_2] \qquad (I)$$

$$\text{OCS formation rate} = \Phi_{CS}\, j_{es}[CS_2] \left(\frac{k_{6a}[O_2] + k_{7a}[O_3]}{k_6[O_2] + k_7[O_3]} \right)$$

$$= \Phi_{CS}\, j_{es}[CS_2]\, \Phi_{OCS} \qquad (II)$$

$$SO_2 \text{ formation rate} = \Phi_{CS}\, j_{es}[CS_2](2 - \Phi_{OCS}) + k_9[OH][OCS]. \qquad (III)$$

There is insufficient experimental data available to allow accurate determination of either Φ_{CS} or Φ_{OCS}. Hence, in the calculations discussed below, both parameters were varied over considerable ranges — $0.01 \leq \Phi_{CS} \leq 0.1$ and $0.1 \leq \Phi_{OCS} \leq 1.0$. The limits were chosen to bracket the range of reasonable values (based on sparse measurement and laboratory data). While we cannot preclude the possibility that $\Phi_{CS} \leq 0.01$, results are not presented for this case because a) the calculated CS_2 profile would be inconsistent with recent measurements [Shalaby, et al, 1980] and b) photooxidation would not be a significant source of OCS.

Model Calculations

To evaluate the potential role of CS_2 photooxidation in tropospheric sulfur chemistry, we have carried out a series of sensitivity calculations using a one-dimensional steady state model, which couples vertical transport and tropospheric photochemistry. Vertical transport was parameterized using the standard eddy diffusion approximation, with a constant diffusion coefficient of 1 × 10^5 cm^{-2}s^{-1}. Ambient conditions appropriate for the remote marine atmosphere at a latitude of 30° at equinox were adopted from Oort and Rasmusson [1970] and the U.S. Standard Atmosphere, 1976.

Table I. Model Calculation Parameters

Model No.	Φ_{CS}	Φ_{OCS}	τ_{OCS} (years)
1	0.1	1.0	1
2	0.05	1.0	1
3	0.01	1.0	1
4	0.1	0.1	1
5	0.01	0.1	1
6	0.1	1.0	2

Concentration profiles of CS_2, OCS, and SO_2 were calculated for varying values of Φ_{cs}, Φ_{ocs}, and τ_{ocs} (the OCS atmospheric lifetime) as summarized in Table I. Because the reaction of SO_2 with OH is a major loss pathway for SO_2 [Davis, et al, 1979], calculation of the SO_2 profile requires knowledge of the atmospheric abundance of OH. The OH profile used in our calculation was generated using the model of Chameides and Tan [1981].

The calculated CS_2 profiles illustrated in Figure 2 were obtained by assuming a balance between a surface source, vertical transport, and loss via photooxidation. In all calculations, the CS_2 abundance at 0 km was fixed at 20 pptv. However, we note that the background surface CS_2 concentration has not yet been reliably established, although measurements over North America appear to suggest a value of about 5-30 pptv [Maroulis and Bandy, 1980; Shalaby, et al, 1980]. Since all the sulfur profiles presented here scale linearly with CS_2, our results may be easily modified as future measurements more accurately define the global CS_2 abundance. The surface flux necessary to support the calculated CS_2 profiles was found to range from 9×10^7 to 3.5×10^8 molecules $cm^{-2}s^{-1}$; this flux is equivalent to a global CS_2 source strength of 1.8 to 6.9 teragrams per year.

The major feature of the calculated CS_2 profiles shown in Figure 2 is the rapid decrease in $[CS_2]$ with increasing altitude. This vertical gradient is indicative of the rapid removal of CS_2 by the proposed photooxidation mechanism as CS_2 is transported upward from the surface source. It should be noted that as Φ_{cs} is decreased, thereby increasing the CS_2 photochemical lifetime, the vertical gradient in CS_2 becomes somewhat less pronounced. In this regard, Shalaby, et al's [1980] recent finding that CS_2 levels in the free troposphere were immeasurably small while CS_2 in the boundary layer was about 8-20 pptv, appears to support a value for Φ_{cs} significantly larger than 0.01.

We believe that the CS_2 sink due to photooxidation may be sufficiently rapid to cause the large spatial and temporal variations in CS_2 concentrations observed by Maroulis and Bandy [1980]. Just as the short lifetime of CS_2 due to photooxidation leads to a rapid decrease in CS_2 in the vertical in our one-dimensional simulations, this process can also cause a rapid fall-off in CS_2 levels in the horizontal direction as one travels away from source regions.

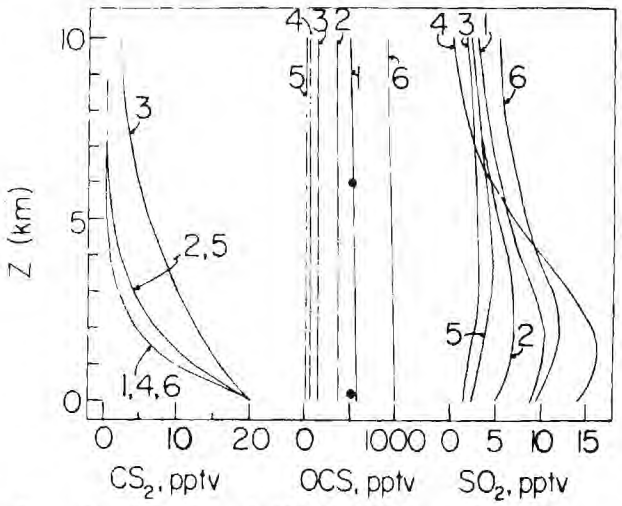


Fig. 2. Calculated (CS_2), (OCS), and (SO_2) altitude profiles. Profile numbers refer to the choice of parameters summarized in Table 1. The filled circles in the OCS plot indicate the averaged OCS levels observed by Torres, et al (1980) in the boundary layer and free troposphere. Note that the only sources of OCS and SO_2 included in these calculations were from CS_2 photooxidation (i.e., Eqn. II) and CS_2 photooxidation (i.e., Eqn. III), respectively.

In the case of OCS, we have, for simplicity, assumed the only source to be via CS_2 photooxidation (i.e., Reactions (2), (3a), and (6a)), while sinks include oceanic hydrolysis [Rowland, 1979] and Reaction (9) with OH. The lifetime of OCS against hydrolysis in the ocean is uncertain and while we have generally adopted a value of one year for this parameter, we have used a value of two years in Model 6 to illustrate the sensitivity of our calculations to the value of this lifetime. Our ability to account for a significant fraction, if not all, of the observed atmospheric OCS abundance (see Figure 2) via CS_2 photooxidation, indicates that this mechanism is potentially a major tropospheric source of OCS. This conclusion, however, is critically dependent upon the assumption that background CS_2 levels are in the 10-20 pptv range and does not preclude the likelihood that other non-photochemical OCS sources [cf. Turco, et al, 1980] also contribute significantly to the global OCS budget. Note that only in Model 5 where both Φ_{cs} and Φ_{ocs} are assigned their minimum values does the calculated OCS mixing ratio (< 10 pptv) become negligible compared to the measured concentrations (~ 500 pptv). On the other hand, in Model 6 we actually calculated more OCS than is observed in the atmosphere.

CS_2 photooxidation appears to be only a minor source for SO_2 in the natural troposphere. The SO_2 profiles illustrated in Figure 2 were obtained by assuming the SO_2 sources were governed by Equation (III) (involving CS_2 photooxidation and OCS oxidation by OH). The sinks for SO_2 included reaction with OH [Atkinson, et al, 1976; Davis, et al, 1979; Harris, et al, 1980], heterogeneous removal with a 5-day lifetime in the boundary layer and a 20-day lifetime in the free troposphere, and loss at the ocean surface with a deposition velocity of 0.5 cm s^{-1} [Liss and Slater, 1974]. As indicated in Figure 2, the CS_2–OCS sources only generate about 1-20 pptv of SO_2 in the boundary layer and 1-10 pptv in the free troposphere. Only if Φ_{cs} is very high and Φ_{ocs} very low can SO_2 levels generated from CS_2 approach the measured concentration of 54 ± 19 pptv in the marine boundary layer [Maroulis, et al, 1980b]. Because of the rapid fall-off in CS_2 levels with altitude, this mechanism cannot (for any combination of Φ_{cs} and Φ_{ocs}) account for a significant fraction of the free tropospheric SO_2 levels of 85 ± 28 pptv measured by Maroulis, et al [1980b].

Conclusions

We conclude from the above analysis that CS_2 photooxidation is probably an important tropospheric sink for the CS_2 giving a lifetime on the order of a week or two. If background CS_2 levels are 10-20 pptv, then CS_2 photooxidation may be an important global source of OCS as well. However, these conclusions are based on rather limited experimental evidence. No direct, real-time kinetic data is available to check the proposed CS_2 photooxidation mechanism. The yields Φ_{cs} and Φ_{ocs}, which are crucial to an assessment of the atmospheric relevance of CS_2 photooxidation, remain poorly defined, as does the tropospheric lifetime of OCS. The dependence of Φ_{cs} on excitation wavelength has not been examined at all. Further investigations aimed at better defining Φ_{cs}, Φ_{ocs}, and τ_{ocs} are needed.

Acknowledgements

This work was supported by the National Science Foundation through Grants No. ATM-78-10092 and ATM-80-19040 (PHW and ARR) and by the National Aeronautics and Space Administration through Grant No. NAG-1-85 (WLC). C. A. Gump and N. M. Kreutter assisted in the absorption cross section measurements. The authors thank Dr. A. R. Bandy for helpful discussions.

References

Arveson, J. C., R. N. Griffin, Jr., and B. D. Pearson, Jr., Determination of extraterrestrial solar spectral irradiance from a research aircraft, Appl. Opt., 11, 2215-2232, 1969.

Atkinson, R., R. A. Perry, and J. N. Pitts, Jr., Rate constants for the reactions of the OH radical with NO_2 (M = Ar and N_2) and SO_2 (M = Ar), J. Chem. Phys., 65, 306-310, 1976.

Baulch, D. L., R. A. Cox, R. F. Hampson, Jr., J. A. Kerr, J. Troe, and R. T. Watson, Evaluated kinetic and photochemical data for atmospheric chemistry, J. Phys. and Chem. Ref. Data, 9, 295-471, 1980.

Brus, L. E., Two exponential decay of 3371Å laser excited CS_2 fluorescence, Chem. Phys. Lett., 12, 116-119, 1971.

Chameides, W. L., and A. Tan, The two-dimensional diagnostic model for tropospheric OH: An uncertainty analysis, J. Geophys. Res., in press, 1981.

Crutzen, P. J., The possible importance of CSO for the sulfate layer of the stratosphere, Geophys. Res. Lett., 3, 73-76, 1976.

Davis, D. D., A. R. Ravishankara, and S. Fischer, SO_2 oxidation via the hydroxyl radical: Atmospheric fate of HSO_3 radicals, Geophys. Res. Lett., 6, 113-116, 1979.

deSorgo, M., A. J. Yarwood, O. P. Strausz, and H. E. Gunning, The photolysis of carbon disulfide and carbon disulfide-oxygen mixtures, Can. J. Chem., 43, 1886-1891, 1965.

Hanst, P. L., L. L. Speller, D. M. Watts, J. W. Spence, and M. F. J. Miller, Infrared measurements of fluorocarbons, carbon tetrachloride, carbonyl sulfide, and other atmospheric trace gases, JAPCA, 25, 1220-1226, 1975.

Harris, G. W., R. Atkinson, and J. N. Pitts, Jr., Temperature dependence of the reaction OH + SO_2 + M $\longrightarrow$ HSO_3 + M for M = Ar and SF_6, Chem. Phys. Lett., 69, 378-382, 1980.

Heicklen, J., The fluorescence of carbon disulfide vapor, J. Amer. Chem. Soc., 85, 3562-3565, 1963.

Iyer, R. S. and F. S. Rowland, A significant upper limit for the rate of formation of OCS from the reaction of OH with CS_2, Geophys. Res. Lett., 7, 797-800, 1980.

Jungen, Ch., D. N. Malm, and A. J. Merer, Analysis of $a^1\Delta_g - {}^1\Sigma_g^+$ transition of CS, in the near ultraviolet, Can. J. Phys., 51, 1471-1490, 1973.

Kurylo, M. J., Flash photolysis resonance fluorescence investigation of the reactions of OH radicals with OCS and CS_2, Chem. Phys. Lett., 58, 238-242, 1978.

Lambert, C. and G. H. Kimbell, The fluorescence of CS_2 vapor, Can. J. Chem., 51, 2601-2608, 1973.

Liss, P. S. and P. G. Slater, Flux of gases across the air-sea interface, Nature, 247, 181-182, 1974.

Logan, J. A., M. B. McElroy, S. C. Wofsy, and M. J. Prather, Oxidation of CS_2 and COS: Sources for atmospheric SO_2, Nature, 281, 185-188, 1979.

Maroulis, P. J. and A. R. Bandy, Measurements of atmospheric concentrations of CS_2 in the eastern United States, Geophys. Res. Lett., 7, 681-684, 1980a.

Maroulis, P. J., A. L. Torres, A. B. Goldberg, and A. R. Bandy, Atmospheric SO_2 measurements on project GAMETAG, J. Geophys. Res., 85, 7345-7349, 1980b.

Olszyna, K. J. and J. Heicklen, The reaction of ozone with carbon disulfide, J. Phys. Chem., 74, 4188-4198, 1970.

Oort, A. H. and E. M. Rasmusson, Atmospheric Circulation Statistics, NOAA Prof. Pap. 5, U.S. Gov't. Printing Office, Washington, D.C., 323 pp., 1970.

Ravishankara, A. R., N. M. Kreutter, R. C. Shah, and P. H. Wine, Rate of Reaction of OH with COS, Geophys. Res. Lett., 7, 861-864, 1980.

Richardson, R. J., CS-O_2 flame reaction chemistry, J. Phys. Chem., 79, 1153-1158, 1975.

Rowland, F. S., The atmospheric and ocean sinks for carbonyl sulfide, 4th International Conference of the Commission on Atmospheric Chemistry and Global Pollution, Boulder, Colo., Abstract IV-6, August 1979.

Sandalls, F. J. and S. Penkett, Measurements of carbonyl sulphide and carbon disulphide in the atmosphere, Atmos. Environ., 11, 197-199, 1977.

Shalaby, L., P. J. Maroulis, and A. R. Bandy, Evidence of a short atmospheric lifetime for carbon disulfide, Geophys. Res. Lett., to be submitted, 1981.

Silvers, S. J. and M. R. McKeever, Time and frequency resolution of CS_2 fluorescence excited by a nitrogen laser, Chem. Phys., 18, 333-339, 1976.

Sze, N. D. and M. K. W. Ko, Is CS_2 a precursor for atmospheric COS?, Nature, 278, 731-732, 1979a.

Sze, N. D. and M. K. W. Ko, CS_2 and COS in the stratospheric sulfur budget, Nature, 280, 309-310, 1979b.

Torres, A. L., P. J. Maroulis, A. B. Goldberg, and A. R. Bandy, Atmospheric OCS measurements on project GAMETAG, J. Geophys. Res., 85, 7357-7360, 1980.

Turco, R. P., R. C. Whitten, O. B. Toon, J. B. Pollack, and P. Hamill, OCS, stratospheric aerosols and climate, Nature, 283, 283-286, 1980.

Wine, P. H., R. C. Shah, and A. R. Ravishankara, Rate of reaction of OH with CS_2, J. Phys. Chem., 84, 2499-2503, 1980.

Wood, W. P. and J. Heicklen, The photooxidation of carbon disulfide, J. Phys. Chem., 75, 854-860, 1971.

(Received November 11, 1980;
accepted April 14, 1981.)

APPENDIX III

Abstract for the Paper

KINETICS OF OH REACTIONS WITH TROPOSPHERIC SULFUR COMPOUNDS

Presented at the 2nd Symposium on the Composition of the Non-urban Troposphere, Williamsburg, Virginia, May 1982, paper 9.1.

KINETICS OF OH REACTIONS WITH TROPOSPHERIC SULFUR COMPOUNDS

P. H. Wine and A. R. Ravishankara
Georgia Institute of Technology
Atlanta, Georgia 30332

1. INTRODUCTION

The tropospheric sulfur cycle has been the subject of intensive investigation in recent years because of the need to assess the contribution of anthropogenically produced sulfur to acid rain, visibility reduction, and climate modification. In most cases, oxidation of sulfur compounds in the troposphere is initiated by OH radical attack. Kinetic data are now available for OH reactions with a number of volatile sulfur compounds. However, all direct studies have been carried out at sub-ambient pressures and/or in the absence of O_2. Only indirect measurements of rate constants have been reported under atmospheric conditions of pressure and gas composition. Two reactions where discrepancies exist between direct measurements and indirect measurements in one atmosphere of air are

$$OH + CH_3SH \rightarrow \text{Products} \qquad (1)$$

and

$$OH + CS_2 \rightarrow \text{Products} . \qquad (2)$$

Cox and Sheppard (1980) have employed a competitive kinetics technique using OH + C_2H_4 as the reference reactions (k_{ref} = 8×10^{-12}cm^{3}molecule^{-1} s^{-1}) to measure k_1 and k_2 in one atm air at 297K. Their result for k_1, $(9.04\pm0.85)\times10^{-11}$cm^3 molecule^{-1}s^{-1}, is nearly a factor of three faster than the flash photolysis-resonance fluorescence (FP-RF) results reported by Atkinson, et al (1977) and Wine, et al (1981). Both FP-RF studies employed argon as the buffer gas with P $\leq$ 120 Torr. In the case of reaction (2), Cox and Sheppard report $k_2 = (4.3\pm1.6)\times10^{-13}$cm^3 molecule^{-1}s^{-1}; while Wine, et al (1980) and Iyer and Rowland (1980) obtained the results $k_2 \leq 1.5\times10^{-15}$ and $k_2 \leq 3\times10^{-15}$ cm^{3}molecule^{-1}s^{-1}, respectively, under oxygen free conditions with 60 Torr SF_6 (Wine, et al) or 70 Torr CS_2+CO (Iyer and Rowland) buffer gas. The available data for k_1 suggests the importance of a pressure dependent channel under tropospheric conditions. A similar explanation does not seem capable of explaining the much larger difference between measured values for k_2. Burrows and Cox [private communication] have suggested that the existing data for k_2 is consistent with a complex mechanism involving reaction of an initially formed OH-CS_2 complex with O_2. In order to elucidate the mechanisms of reactions (1) and (2) and facilitate proper choice of rate constants for modeling purposes we have undertaken an investigation of the pressure and [O_2] dependence of k_1 and k_2. Simultaneously, we are also studying the pressure and temperature dependence of the rate constant for the reaction

$$OH + SO_2 + M \rightarrow HSO_3 + M,\ M = Ar, N_2, SF_6. \qquad (3)$$

Reaction (3) is now thought to be the dominant homogeneous SO_2 oxidation pathway in both the urban and non-urban troposphere, although it should be pointed out that the potential importance of the CH_3O_2+SO_2 reaction remains a controversial issue [Kan (1981), Sander (1981].

Some initial results from our studies of reactions (1)-(3) are presented in this paper.

2. EXPERIMENTAL

The flash photolysis-resonance flourescence technique was employed in all experiments. The application of this technique to the study of OH reactions with atmospheric sulfur compounds has been described in previous publications [Wine (1980,1981); Ravishankara (1980)]. In the present study it was necessary to tailor the spectral distribution of the photoflash so as to produce OH under conditions where the concentrations of other reactive photofragments were small; otherwise secondary reactions involving these photofragments would become dominant. In all experiments where the reaction mixture conatined either CS_2 or O_2, OH was produced by 248 nm KrF laser photolysis of H_2O_2 or HNO_3. Some studies of reaction (1) in the absence of O_2 and all investigations of reaction (3) employed broadband flash photolysis of H_2O at wavelengths greater than 165 nm as the source of OH. Over the range of flash energies and species concentrations employed, no evidence for complicating secondary chemistry was observed in the study of reaction (1). However, in the case of reaction (3), both an interfering chemiluminescent signal and secondary production of OH were observed when high SO_2 concentrations were employed Both of these complications resulted from secondary chemistry involving the SO_2 photofragments SO and O(^{3}P). To suppress the production of these reactive species, the photoflash was filtered with up to 50 Torr-cm SO_2. The SO_2 absorption cross section is smaller than the H_2O cross section over the wavelength range (165-185 nm) where most H_2O photolysis occurs but is very large in the 190-220 nm region. Hence, use of an SO_2 filter resulted in a large decrease in the levels of SO and O(^{3}P) but only a small decrease in the OH concentration.

Because O_2 quenches OH resonance fluorescence very efficiently, the results reported in this paper are limited to O_2 partial pressures of a few Torr. Modifications in the OH detection technique will be required in order to extend these experiments to O_2 levels typical of the lower troposphere.

The gases used in this study had the following stated purities: CH_3SH > 99.5%, SO_2>99.98%, O_2>99.99%, SF_6>99.99%, and Ar>99.9995%. Both CH_3SH and SO_2 were subjected to repeated freeze (77K)-pump-thaw cycles before use. O_2, SF_6, and Ar were used as supplied. The CS_2 sample was Fischer ACS reagent grade. It was purified by trap-to-trap distillation (210-77K) followed by repeated degasing at 77K.

3. RESULTS AND DISCUSSION

All experiments were carried out under pseudo-first order conditions with the reactant R (R ≡ CH_3SH, CS_2, SO_2) in large excess over OH. Under conditions where OH is removed from the detection zone only by reaction with R, diffusion, and reaction with background impurities and/or the OH photolytic precursor, the OH temporal profile is defined by the relationship

$$[OH]_t = [OH]_o \exp(-k't) \qquad (4)$$

where k' is the pseudo-first order rate constant for OH removal:

$$k' = k_i[R_i] + k_j[P_j] + k_d \ . \qquad (5)$$

In equation (5), k_i is the bimolecular rate constant for reaction of OH with the reactant R_i, k_j is the bimolecular rate constant for the reaction of OH with the photolytic precursor P_j, and k_d is the first order rate constant for removal of OH by diffusion from the field of view of the detector and reaction with background impurities. Both k_i and k_j can depend upon temperature, pressure, and the identity of the buffer gas. For a specified set of $[R_i]$, $[P_j]$, pressure, and temperature, k' is determined from the slope of a $-\ln S_t$ vs. t plot (S_t ≡ the resonance fluorescence signal at time t). The desired bimolecular rate constant is then determined from the dependence of k' on $[R_i]$ at fixed $[P_j]$, temperature, and pressure.

The results obtained for each reaction are discussed individually below.

OH + CH_3SH → products

The results obtained for reaction (1) are summarized in Table 1. Within experimental uncertainties no dependence of k_1 on pressure or $[O_2]$ is observed. The average of the five rate constants reported in Table 1, $k_1 = 3.18 \times 10^{-11}$ $cm^3 molecule^{-1} s^{-1}$, is in good agreement with the previous FP-RF results of Atkinson, et al (1977) and Wine, et al (1981). Since SF_6 is a more efficient third body than air, the observation of no pressure dependence for k_1 over the range 25-200 Torr SF_6 effectively eliminates the possibility that formation and stabilization of a reaction complex results in k_1 being faster at P = 1 atm than at P ∿ 50 Torr. However, further experiments are needed with various O_2/M mixture before an $[O_2]$ dependence can be definitively rejected as a possibility.

Table 1

Rate constants for the reaction OH+CH_3SH → products. T = 298±1K.

OH Production Mechanism*	Buffer Gas/ Pressure (Torr)	O_2 Partial Pressure (Torr)	$k_1 \pm 2\sigma$† (10^{-11} $cm^3 molecule^{-1} s^{-1}$)
1	25/SF_6	0	3.25 ± 0.09
1	200/SF_6	0	3.09 ± 0.10
1	80/Ar	0	3.04 ± 0.19
2	100/Ar	0	3.47 ± 0.12
2	100/Ar	3.0	3.06 ± 0.22

* 1: broadband flash photolysis of H_2O at λ > 165 nm; 2: KrF laser photolysis of HNO_3

† Errors refer to precision only

OH + CS_2 → products

The studies of reaction (2) were extremely signal limited because both CS_2 and O_2 quench OH resonance fluorescence very efficiently. The experiments reported here were aimed primarily at determining qualitatively whether or not the reaction rate is enhanced by the presence of O_2. For this reason SF_6, which is very efficient at stabilizing collision complexes, was employed as the buffer gas in all experiments. In agreement with our earlier study (Wine (1980)], the reaction was found to be very slow in the absence of O_2. When 1-3 Torr O_2 was added to the reaction mixture, a pronounced increase in k_2 was observed. k_2 was also found to increase with decreasing temperature; this suggests that the initial step in the reaction mechanism is formation of an OH...CS_2 complex.

Table 2

Rate constants for the reaction OH+CS_2 → products. The buffer gas was SF_6 in all experiments. OH was produced by KrF laser photolysis of H_2O_2.

T(K)	P(Torr)	P_{O_2} (Torr)	$k_2 \pm 2\sigma$† (10^{-15} $cm^3 molecule^{-1} s^{-1}$)
298	100	0	< 1
298	250	0	< 5
298	250	1.2	29 ± 4
298	250	3.3	51 ± 17
298	500	1.0	32 ± 7
259	250	0	7 ± 3
259	250	1.2	110 ± 50

† Errors refer to precision only

OH + SO_2 → products

At this time we have completed a study of the temperature and pressure dependence of k_3 for M = SF_6. The results are summarized in Table 3. Calvert, et al (1978) reviewed the data base available at the time and recommended a value of 1.1 x 10^{-12} $cm^3 molecule^{-1} s^{-1}$ for k_3 at 298K and 1 atm air. Since then, new data have been reported by Davis, et al (1979) and Harris, et al (1980);

these data suggest a slightly lower value for k_3 —in the range 9-10 x 10^{-13} $cm^3 molecule^{-1} s^{-1}$. Our results for M = SF_6 are typically ∿ 20% lower than those reported by Harris, et al, and thus suggest a value of ∿ 8 x 10^{-13} $cm^3 molecule^{-1} s^{-1}$ for k_3 at 298K and 1 atm air. Further experiments with M = Ar and N_2 are in progress.

Table 3

Rate constants for the reaction $OH+SO_2+SF_6$. Units are 10^{-13} $cm^3 molecule^{-1} s^{-1}$; Errors are 2σ and represent precision only.

$[SF_6]$ (10^{17} molecule cm^{-3}) \ T(K)	260	300	360	420
5.0	2.96 ± 0.11	1.92 ± 0.20	1.29 ± 0.09	1.07 ± 0.04
10.0	3.70 ± 0.30	2.97 ± 0.13	2.18 ± 0.17	1.51 ± 0.11
20.0	5.68 ± 0.46	4.38 ± 0.35	2.63 ± 0.30	2.19 ± 0.15
40.0	7.31 ± 0.60	5.27 ± 0.15	4.38 ± 0.24	3.71 ± 0.41
80.0	9.50 ± 0.86	7.17 ± 0.30	5.83 ± 0.33	4.91 ± 0.50
160	12.4 ± 1.4	9.66 ± 0.80	7.45 ± 0.85	7.19 ± 0.70

4. CONCLUSIONS

The following conclusions can be drawn from the results presented in this paper:

(1) k_1 is independent of pressure if the buffer gas is chemically inert (i.e. Ar, N_2, or SF_6 but not necessarily O_2).

(2) Reaction (2) becomes much faster when a few Torr O_2 are added to the reaction mixture. The large difference in rate constants reported by Cox and Sheppard (1980) vs. Wine, et al (1980) and Iyer and Rowland (1980) appears to be attributable to the dependence of k_2 on $[O_2]$.

(3) Reaction (3) appears to be a little slower under atmospheric conditions than current evaluations suggest.

Quantitative assessment of the $[O_2]$ dependence of k_1 and k_2 (and for that matter, k_3 as well) at O_2 levels found in the troposphere will require vast improvement in OH detection sensitivity. An apparatus featuring pulsed laser induced fluorexcence detection of OH is being constructed in our laboratory, and is expected to be "on line" soon. This apparatus provides the sensitivity needed to monitor OH kinetically under the desired conditions.

5. ACKNOWLEDGEMENTS

We would like to thank D. H. Semmes and C. A. Gump for assisting with some of the experiments. This work was supported by the National Science Foundation under grant No. ATM-80-19040.

6. REFERENCES

Atkinson, R., R. A. Perry, and J. N. Pitts, Jr., 1977: Rate constants for the reaction of the OH radical with CH_3SH and CH_3NH_2 over the temperature range 299-426K. J. Chem. Phys., 66, 1578-1581.

Calvert, J. G., F. Su, J. W. Bottenheim and O. P Strausz, 1978; Mechanism of the homogeneous oxidation of sulfur dioxide in the troposphere Atmos. Environ., 12, 197-226.

Cox, R. A. and D. Sheppard, 1980: Reactions of OH radicals with gaseous sulfur componds, Nature, 284, 330-331.

Davis, D. D., A. R. Ravishankara and S. Fischer, 1979: SO_2 oxidation via the hydroxyl radical: atmospheric fate of HSO_x radicals. Geophys. Res. Lett., 6, 113-116.

Harris, G. W., R. Atkinson and J. N. Pitts, Jr., 1980: Temperature dependence of the reaction $OH+SO_2+M \rightarrow HSO_3+M$ for M = Ar and SF_6. Chem. Phys. Lett., 69, 378-382.

Iyer, R. S. and F. S. Rowland, 1980: A significant upper limit for the rate of formation of OCS from the reaction of OH with CS_2. Geophys. Res. Lett., 7, 797-800.

Kan, C. S., J. G. Calvert and J. H. Shaw, 1981: Oxidation of sulfur dioxide by methylperoxy radicals. J. Phys. Chem., 85, 1126-1132.

Ravishankara, A. R., N. M. Kreutter, R. C. Shah and P. H. Wine, 1980: Rate of reaction of OH with COS. Geophys. Res. Lett., 7, 861-864.

Sander, S. P. and R. T. Watson, 1981: A kinetics study of the reaction of SO_2 with CH_3O_2. Chem. Phys. Lett., 77, 473-475.

Wine, P. H., R. C. Shah and A. R. Ravishankara, 1980: Rate of reaction of OH with CS_2. J. Phys. Chem., 85, 2499-2503

Wine, P. H., N. M. Kreutter, C. A. Gump and A. R. Ravishankara, 1981: Kinetics of OH reactions with the atmospheric sulfur compounds H_2S, CH_3SH, CH_3SCH_3, and CH_3SSCH_3. J. Phys. Chem., 85, 2660-2665.

APPENDIX IV

Summary of unpublished data on

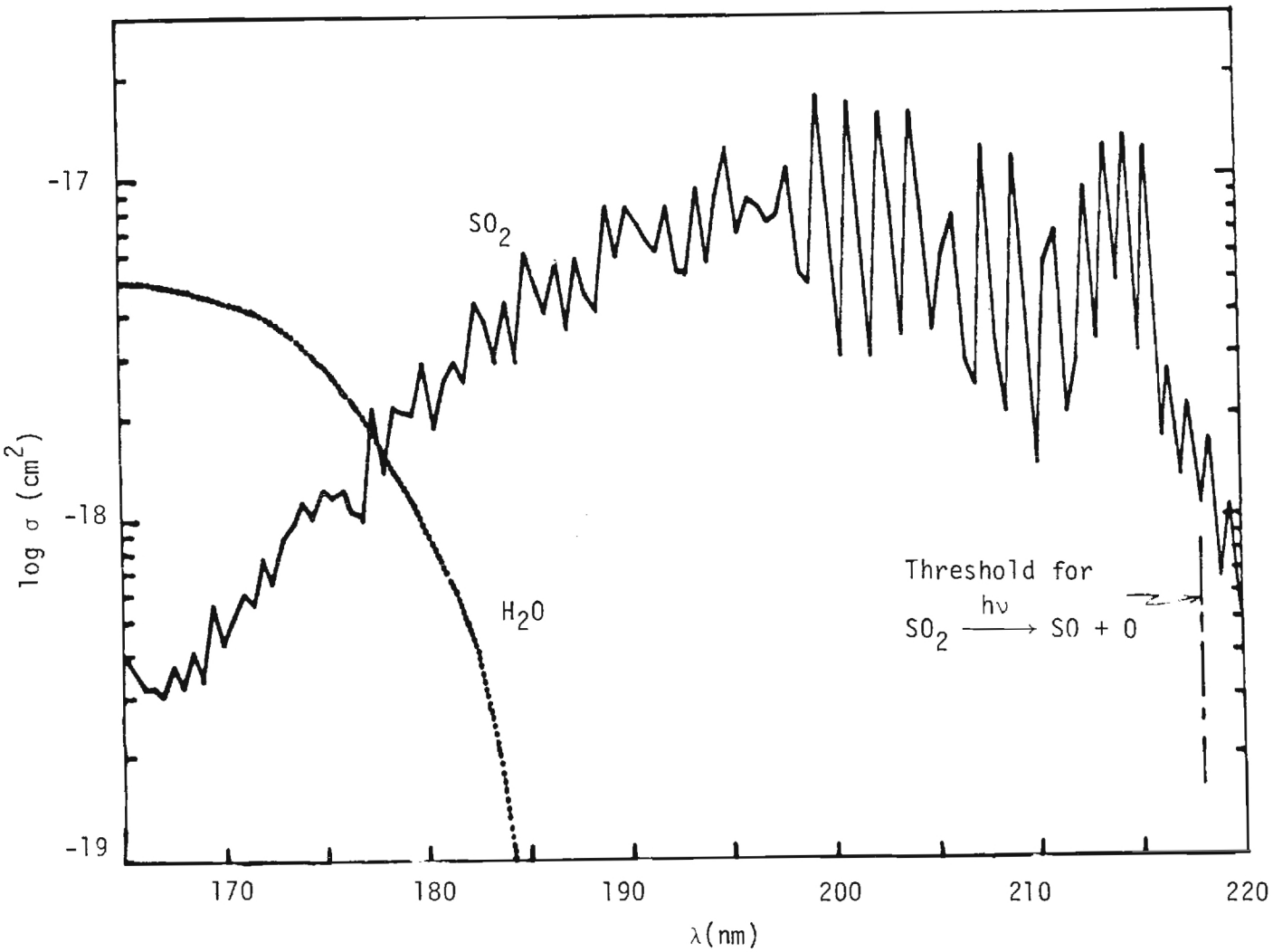
RATE CONSTANTS FOR THE REACTION OH + SO_2 + M $\longrightarrow$ HSO_3 + M AS A FUNCTION OF TEMPERATURE AND PRESSURE

To be published in the Journal of Physical Chemistry

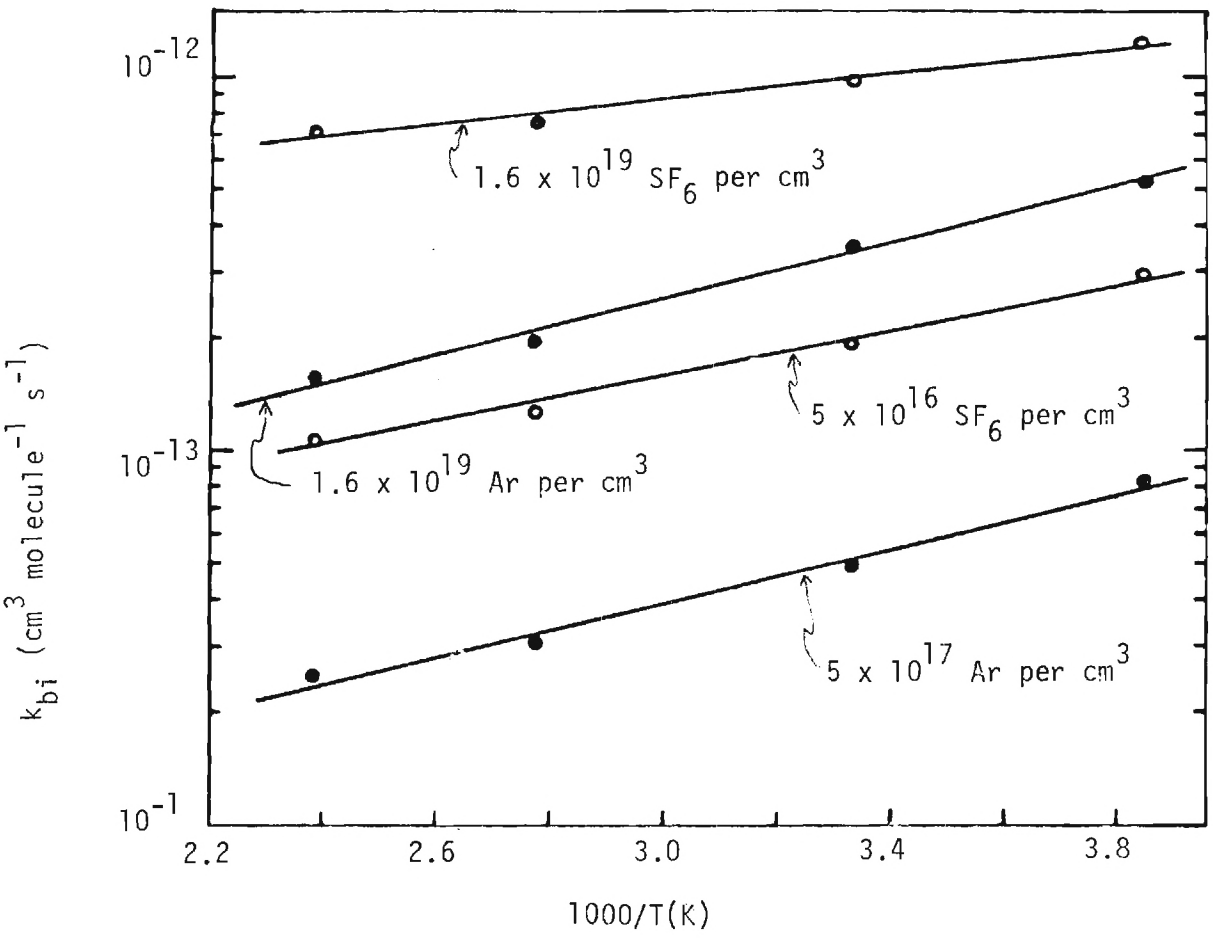
RATE CONSTANTS FOR THE REACTION OH + SO_2 + M ——→ HSO_3 + M

$[M](10^{17}cm^{-3})$	M	$k(10^{-14}cm^3molecule^{-1}s^{-1})$			
		260K	300K	360K	420K
5	He		4.67 ± 0.28		
	Ar	8.21 ± 0.53	4.91 ± 0.48	3.03 ± 0.38	2.51 ± 0.24
	N_2		11.4 ± 1.4		
	SF_6	29.6 ± 1.1	19.2 ± 2.0	12.9 ± 0.9	10.7 ± 0.4
10	He		6.90 ± 0.70		
	Ar	11.8 ± 0.9	7.85 ± 0.50	4.35 ± 0.38	3.78 ± 0.23
	N_2		17.9 ± 2.0		
	SF_6	37.0 ± 3.0	29.0 ± 2.0	21.8 ± 1.7	15.1 ± 1.1
20	He		10.3 ± 0.9		
	Ar	16.7 ± 0.9	12.1 ± 0.6	6.22 ± 0.29	4.90 ± 0.41
	N_2		28.4 ± 4.0		
	SF_6	56.8 ± 5.0	43.8 ± 3.1	28.6 ± 2.2	21.9 ± 2.0
40	He		14.4 ± 1.0		
	Ar	23.6 ± 1.6	15.8 ± 1.3	9.59 ± 0.88	7.22 ± 0.45
	SF_6	73.1 ± 7.3	52.2 ± 2.0	43.8 ± 2.4	37.1 ± 4.1
80	He		21.1 ± 1.5		
	Ar	36.5 ± 3.1	23.4 ± 2.1	13.4 ± 0.6	10.7 ± 0.9
	SF_6	95.0 ± 8.6	71.7 ± 3.5	58.3 ± 3.3	49.1 ± 5.0
160	He		34.0 ± 2.0		
	Ar	52.8 ± 5.3	36.8 ± 4.5	19.2 ± 2.3	15.8 ± 1.5
	SF_6	124 ± 14	100 ± 10	74.5 ± 8.5	71.9 ± 8.0

Errors are 2σ are refer to precision only

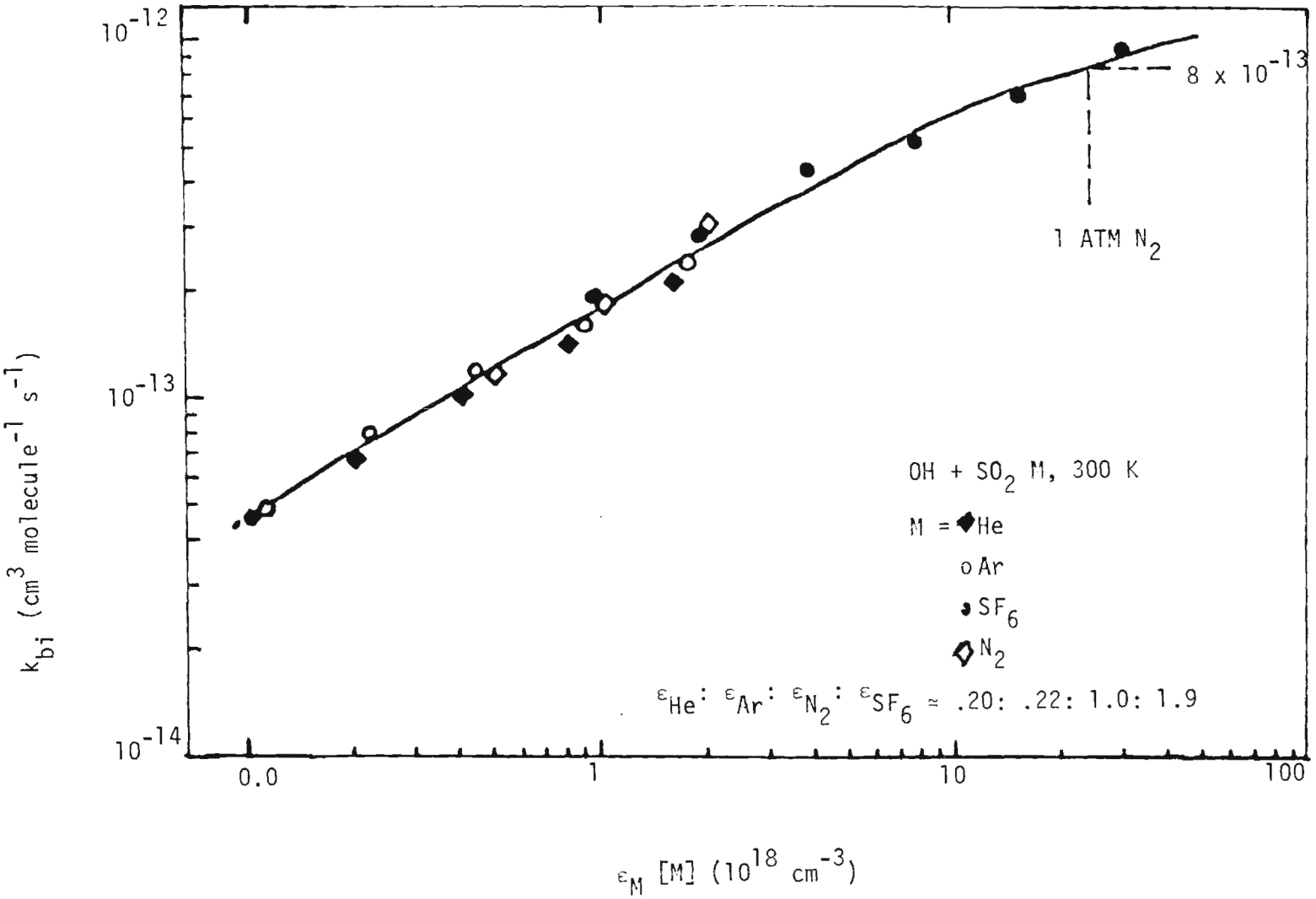


OH produced by flash photolysis of H_2O. SO_2 filter used to prevent photolysis of SO_2 in 180-220 nm region.



Temperature dependences shown in Arrhenius form.

M	[M]	Arrhenius Expression (cm^3 $molecule^{-1}$ s^{-1})
Ar	5 x 10^{17}	(3.3 ± 1.6) x 10^{-15} exp [(820 ± 150)/T]
Ar	1.6 x 10^{19}	(1.9 ± 0.9) x 10^{-14} exp [(860 ± 140)/T]
SF_6	5 x 10^{17}	(2.0 ± 0.6) x 10^{-14} exp [(690 ± 90)/T]
SF_6	1.6 x 10^{19}	(2.7 ± 1.0) x 10^{-13} exp [(390 ± 120)/T]



Fall-off curve.

APPENDIX V

Reprint of the Paper

UPPER LIMIT FOR THE RATE OF REACTION OF $Cl(^2P)$ WITH METHYL CHLOROFORM

UPPER LIMIT FOR THE RATE OF REACTION OF $Cl(^2P_J)$ WITH METHYL CHLOROFORM

P.H. WINE, D.H. SEMMES and A.R. RAVISHANKARA
Molecular Sciences Group, Engineering Experiment Station, Georgia Institute of Technology, Atlanta, Georgia 30332, USA

Received 10 May 1982

The kinetics of the reaction $Cl(^2P_J) + CH_3CCl_3 \xrightarrow{k_3} \dot{C}H_2CCl_3 + HCl$ has been investigated over the temperature range 259–403 K. $Cl(^2P_J)$ was prepared by 355 nm pulsed laser photolysis of Cl_2 and detected by time-resolved resonance fluorescence. Upper limits for $k_3(T)$ in units of 10^{-14} cm^3 molecule^{-1} s^{-1} are 2.40 at 259 K, 3.68 at 298 K, and 7.74 at 356 K. At 403 K, secondary production of $Cl(^2P_J)$ was observed under all experimental conditions. The title reaction is too slow to be important in atmospheric chemistry.

1. Introduction

CH_3CCl_3 (methyl chloroform) is widely used as an industrial solvent and degreasing agent. Sufficient CH_3CCl_3 is introduced into the atmosphere from anthropogenic sources that the globally averaged tropospheric concentration of this compound now exceeds 100 parts per trillion and is increasing anually [1]. It is generally assumed that the only important chemical sink for CH_3CCl_3 in the troposphere is the reaction

$$OH + CH_3CCl_3 \rightarrow \dot{C}H_2CCl_3 + H_2O\,. \qquad (1)$$

Reaction (1) is relatively slow [2,3]; hence, it is believed that a significant fraction of tropospheric CH_3CCl_3 is transported to the stratosphere, where its photodissociation can contribute to ClO_x – catalyzed destruction of ozone. Based on measurement data from the last several years and a detailed emissions inventory, the tropospheric lifetime of CH_3CCl_3 is estimated to be ≈13 years [1]. This lifetime can be used to deduce an average tropospheric OH concentration if it is assumed that reaction (1) and transport to the stratosphere are the only important sinks for CH_3CCl_3.

The existence of an additional tropospheric sink for CH_3CCl_3 would have two important effects on our current understanding of atmospheric chemistry. First, the flux of CH_3CCl_3 into the stratosphere would be reduced, thereby decreasing the total chlorine available for participation in catalytic ozone destruction cycles. Also, tropospheric OH concentrations deduced from methyl chloroform concentration data would be overestimated. At 220 K, a temperature typical of the upper troposphere, the reaction of $Cl(^2P_J)$ with ethane,

$$Cl(^2P_J) + CH_3CH_3 \rightarrow \dot{C}H_2CH_3 + HCl\,, \qquad (2)$$

is known to be very fast ($k_2 \approx 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 220 K [4]). Since $Cl(^2P_J)$ should react with methyl chloroform by the same mechanism (hydrogen abstraction) as with ethane, it has been suggested [5] that the reaction

$$Cl(^2P_J) + CH_3CCl_3 \rightarrow \dot{C}H_2CCl_3 + HCl \qquad (3)$$

could be an important sink for methyl chloroform in the upper troposphere. Based on calculated $Cl(^2P_J)$ concentrations at 10–15 km [6], if $k_3 > 1 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 220 K, then reaction (3) would be significant. Also, since the stratospheric lifetime of CH_3CCl_3 toward photodissociation is ≈7 years [1], reaction (3) could be a significant methyl chloroform sink in the lower stratosphere if $k_3(220\ \text{K}) > 1 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}.

To investigate the possible role of reaction (3) in atmospheric chemistry, we have studied its kinetics as a function of temperature. Our results are presented in this paper. We find reaction (3) to be surprisingly slow – $k_2 > 1300k_3$ at 298 K.

0 009-2614/82/0000–0000/$ 02.75

2. Experimental

The experimental apparatus was nearly identical to one employed previously in our laboratory to study the reaction of $Cl(^2P_J)$ with CH_4 [7]. A brief description of the apparatus is given below.

A pyrex, jacketed reaction cell with an internal volume of ≈ 150 cm^3 was used in all experiments. The cell was maintained at a constant temperature by circulating ethylene glycol from a thermostatted bath through the outer jacket. A copper–constantan thermocouple with a stainless steel jacket was injected into the reaction zone through a vacuum seal, thus allowing measurement of the gas temperature under the precise pressure and flow rate conditions of the experiment. $Cl(^2P_J)$ was produced by 355 nm laser (Nd : YAG, third harmonic) photolysis of Cl_2. A chlorine resonance lamp situated perpendicular to the photolysis laser excited resonance fluorescence in the photolytically produced atoms. The resonance lamp output was filtered with a calcium fluoride window and an N_2O gas filter to prevent impurity emission of O, N, and H resonance radiation from entering the reactor. Fluorescence was collected at 90° to both the resonance lamp and photolysis laser by a magnesium fluoride lens and imaged onto the photocathode of a solar blind photomultiplier. Signals were obtained by photon counting and then fed into a signal averager operating in the multi-channel scaling mode. For each decay rate measured, sufficient flashes were averaged to obtain a well-defined temporal profile over at least two and usually more than three 1/e times.

In order to avoid the accumulation of photolysis or reaction products, all experiments were carried out under "slow flow" conditions. The linear flow rate through the reactor was 3 cm s^{-1} and the laser repetition rate was 1 Hz. Hence, an essentially "fresh" reaction mixture was available for each laser shot. CH_3CCl_3 reactant was flowed from a 12 ℓ bulb containing a dilute reactant/Ar mixture. Cl_2 was flowed from a cylinder containing a 0.1% mixture of Cl_2 in Ar. The CH_3CCl_3 mixture, Cl_2 mixture, and additional Ar were premixed before entering the reactor. The concentrations of each component in the reaction mixture were determined from measurements of the appropriate mass flow rates and the total pressure. The fraction of CH_3CCl_3 in the CH_3CCl_3/Ar mixture was checked frequently by UV photometry at 185.0 nm (Hg line). The absorption cross section for CH_3CCl_3 at 185.0 nm was measured during the course of the investigation. The result, 2.98×10^{-18} cm^2, is in excellent agreement with the value (2.96×10^{-18} cm^2) reported by Hubrich and Stuhl [8] but is $\approx 11\%$ higher than the value (2.65×10^{-18} cm^2) reported by Vanlaethem-Meureé et al. [9].

The gases used in this study were obtained from Matheson and had the following stated purities: Ar $\geqslant$ 99.9995%, $Cl_2 \geqslant 99.9\%$, and He $\geqslant 99.999\%$; they were used as supplied. An analyzed sample of unstabilized CH_3CCl_3 was provided by Dow Chemical. The overall purity of the sample was 99.88 mole%. Major impurities were CHCl=CHCl (0.061 mole%), $CHCl_2CHCl_2$ (0.050 mole%), and CH_3CHCl_2 (0.013 mole%). The sample was further purified by vacuum distillation with only the middle fraction used in experiments.

3. Results and discussion

All experiments were carried out under pseudo-first order conditions with CH_3CCl_3 in large excess. Argon was used as the buffer gas at a pressure of 100 Torr, thus insuring that a thermal distribution of $Cl(^2P_J)$ spin–orbit states was maintained throughout the course of the reaction [7]. In most experiments the atomic and molecular chlorine concentrations were $[Cl(^2P_J)]_0 \approx 1 \times 10^{11}$ molecules cm^{-3} and $[Cl_2] \approx 3.5 \times 10^{13}$ molecules cm^{-3}. However, at all temperatures investigated some experiments were carried out with first the laser photon flux, then the Cl_2 concentration increased by a factor four. Neither of these variations in experimental conditions influenced the $Cl(^2P_J)$ decay kinetics. We conclude that neither biphotonic processes, such as reaction of $Cl(^2P_J)$ with a product of reaction (3) or with a photolytically produced atom, nor the reaction

$$\dot{C}H_2CCl_3 + Cl_2 \rightarrow CH_2ClCCl_3 + Cl(^2P_J) \qquad (4)$$

were important as $Cl(^2P_J)$ production or removal mechanisms.

To measure k_3 it is desirable to establish experimental conditions where the $Cl(^2P_J)$ temporal profile is governed entirely by the following processes:

$$Cl_2 \xrightarrow[355\ \text{nm}]{h\nu} 2Cl(^2P_J), \qquad (5)$$

$$Cl(^2P_J) + CH_3CCl_3 \rightarrow \dot{C}H_2CCl_3 + HCl\,, \qquad (3)$$

$$Cl(^2P_J) \rightarrow \text{loss by diffusion from the detector field of view and reaction with background impurities.} \qquad (6)$$

Then, since $[CH_3CCl_3] \gg [Cl(^2P_J)]$, the integrated rate equation is

$$\ln\{[Cl(^2P_J)]_0/[Cl(^2P_J]_t\}$$

$$= (k_3[CH_3CCl_3] + k_6)t \equiv k't\,. \qquad (7)$$

Observation of $Cl(^2P_J)$ temporal profiles which are exponential, i.e., obey eq. (7), a linear dependence of k' on $[CH_3CCl_3]$, and the forementioned independence of k' to variations in laser photon flux and $[Cl_2]$ serves as proof that reactions (3), (5), and (6) are, indeed, the only processes which affect the $Cl(^2P_J)$ time history *except* that the possible presence of reactive impurities in the CH_3CCl_3 sample is not elucidated by such a kinetic analysis.

The kinetics of reaction (3) were investigated at the temperatures 259, 298, 356, and 403 K. At the three lowest temperatures all observed temporal profiles were exponential (typical data are shown in fig. 1) and plots of k' versus $[CH_3CCl_3]$ were linear (fig. 2). However, at 403 K, non-exponential $Cl(^2P_J)$ tem-

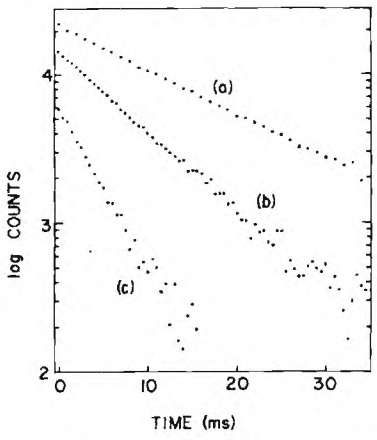


Fig. 1. Typical $Cl(^2P_J)$ temporal profiles observed at $T = 356$ K. Experimental conditions are $T = 356$ K; $[Cl_2] = 3.2 \times 10^{13}$ molecules cm^{-3}; laser energy flux = 20 mJ cm^{-2}; $[CH_3CCl_3]$ in units of 10^{15} molecules cm^{-3} = (a) 0, (b) 0.79, and (c) 2.41; number of laser shots averaged = (a) 32, (b) 120, and (c) 256.

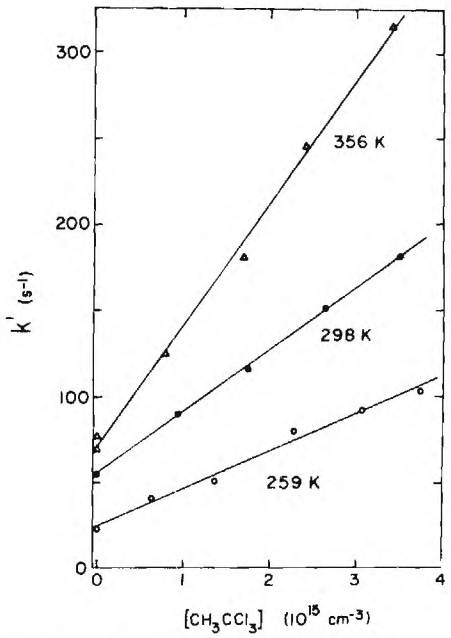


Fig. 2. k' versus $[CH_3CCl_3]$ plots for the data obtained at 259, 298, and 356 K. The solid lines are obtained from unweighted linear least-squares analyses and give the rate coefficients tabulated in table 1.

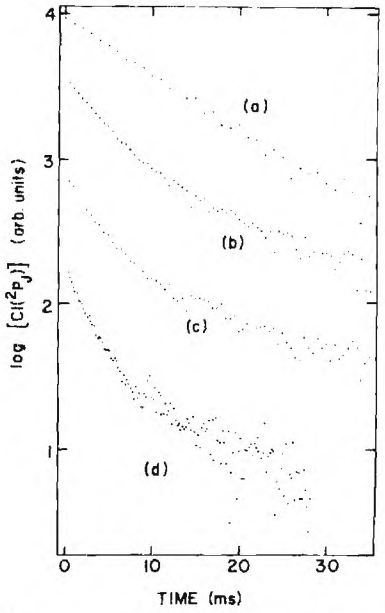


Fig. 3. $CL(^2P_J)$ temporal profiles observed at $T = 403$ K. Experimental conditions are $[Cl_2] = 3.8 \times 10^{13}$ molecules cm^{-3}; laser energy flux = 20 mJ cm^{-2}; $[CH_3CCl_3]$ in units of 10^{15} molecules cm^{-3} = (a) 0, (b) 0.75, (c) 1.41, and (d) 2.04; number of laser shots averaged = (a) 20, (b) 125, (c) 256, and (d) 800.

poral profiles were observed (fig. 3). Apparently, a secondary reaction with a reasonably large activation energy was regenerating $Cl(^2P_J)$ on the time scale of its decay. Two possible secondary reactions which would result in temporal profiles which are independent of variations in $[Cl_2]$ and laser photon flux are

$$\dot{C}H_2CCl_3 \xrightarrow{M} CH_2{=}CCl_2 + Cl(^2P_J) \quad (8)$$

and

$$\dot{C}H_2CCl_3 + CH_3CCl_3 \rightarrow CH_3CCl_2CH_2CCl_3 + Cl(^2P_J)\,. \quad (9)$$

The fact that the observed temporal profiles did not become "more exponential" with increasing k' suggests that reaction (9) was more important than reaction (8). However, a much more detailed analysis would be required to unequivocably identify the source of regenerated $Cl(^2P_J)$.

As discussed above, the CH_3CCl_3 sample with initial purity of 99.88% was vacuum distilled and only the middle fraction was used to prepare CH_3CCl_3/Ar mixtures. Nonetheless, we observed that the apparent bimolecular rate constant decreased as the CH_3CCl_3 sample was used up. Apparently, a significant fraction of $Cl(^2P_J)$ removal which was observed was due to a reactive impurity (probably CHCl=CHCl) whose mole fraction decreased as the sample was used up. The data shown in fig. 2 were obtained with the final remaining aliquot of sample; rate coefficients derived from these data are given in table 1. Because of the secondary chemistry problems encountered at 403 K, a rate coefficient is not reported at that temperature. Clearly, the reported rate coefficients contain a non-negligible contribution from impurity reactions and, therefore, should be considered upper limits for k_3. Taking the measured k_3 ($\equiv k_3^{meas}$) and adding two standard deviations of the least-squares slopes gives the upper limit rate coefficients tabulated in table 1. Elaborate purification procedures, such as those employed in the two most recent studies of reaction (1) [2,3], were not undertaken because an experimental problem, absorption of resonance lamp radiation by CH_3CCl_3, prohibited extension of our measurements to higher CH_3CCl_3 concentration levels.

Table 1
Measured rate coefficients for the reaction of $Cl(^2P_J)$ with CH_3CCl_3. Errors are 2σ and refer to precision only. Units are 10^{-14} cm^3 molecule^{-1} s^{-1}

T (K)	k_3^{meas}	Upper limit for $k_3 \equiv k_3^{meas} + 2\sigma$
259	2.16 ± 0.24	2.40
298	3.58 ± 0.10	3.68
356	7.13 ± 0.51	7.64

The $Cl(^2P_J)$ concentration at 15 km is typically 8×10^2 molecules cm^{-3} [6]. Using our result at 259 K as a conservative upper limit for k_3 at lower temperatures, we obtain the value 2×10^{-11} s^{-1} as a lower limit for the pseudo-first order rate coefficient for removal of CH_3CCl_3 by $Cl(^2P_J)$ at 15 km, i.e. the lifetime of CH_3CCl_3 toward reaction with $Cl(^2P_J)$ is $\geqslant$1500 years. The lifetimes of CH_3CCl_3 toward destruction by OH and transport to higher altitudes followed by photodissociation are $\approx$50 years and $\approx$7 years, respectively. Hence, we conclude that reaction (3) is of negligible importance as a sink for methyl chloroform in the troposphere and lower stratosphere.

The reactivity trend observed in reactions of ethane and methyl chloroform with $Cl(^2P_J)$ is qualitatively similar to the trend observed in reactions of these compounds with $OH(X\,^2\Pi)$, a molecular radical whose electronic structure is similar to that of $Cl(^2P_J)$ – ethane is more reactive than methyl chloroform. However, the reactivity difference is much larger in the case of $Cl(^2P_J)$ reactions than in the case of $OH(X\,^2\Pi)$ reactions. At 298 K, $Cl(^2P_J)$ reacts with ethane at least 1300 times faster than with methyl chloroform whereas the comparable $OH(X\,^2\Pi)$ reaction rate coefficients differ by a factor of 24 [4]. To better understand this unexpected result, we are extending our kinetic measurements to include $Cl(^2P_J)$ reactions with all the mono-, di-, and tri-chloroethanes. The results of this study will be published in the near future.

Acknowledgement

We would like to thank Professor Paul Crutzen for suggesting the potential importance of reaction (3) in atmospheric chemistry. We would also like to thank D. Gerard and S. Collier of Dow Chemical for supplying us with an analyzed sample of unstabilized CH_3CCl_3. This work was supported in part by the

National Aeronautics and Space Administration through subcontract no. 954814 from the Jet Propulsion Laboratory and in part by the National Science Foundation through grant no. ATM-80-19040.

References

[1] F.N. Alyea and D.M. Cunnold, private communication.
[2] K.M. Jeong and F. Kaufman, Geophys. Res. Letters 6 (1979) 757.
[3] M.J. Kurylo, P.C. Anderson and O. Klais, Geophys. Res. Letters 6 (1979) 760.
[4] Chemical Kinetic and Photochemical Data for use in Stratospheric Modelling, Evaluation No. 4, NASA panel for data evaluation, JPL publication 81-3 (1981).
[5] P.J. Crutzen, private communication.
[6] D.J. Wuebbles, private communication.
[7] A.R. Ravishankara and P.H. Wine, J. Chem. Phys. 72 (1980) 25; and references therein.
[8] C. Hubrich and F. Stuhl, J. Photochem. 12 (1980) 93.
[9] N. Vanlaethem-Meureé, J. Wisemberg and P.C. Simon, Geophys. Res. Letters 6 (1979) 757.

APPENDIX VI

Preprint of The Paper

KINETICS OF $Cl(^2P_J)$ REACTIONS WITH THE CHLORETHANES

CH_3CH_2Cl, CH_3CHCl_2, CH_2ClCH_2Cl, AND $CH_2ClCHCl_2$

Journal of Physical Chemistry, in press

KINETICS OF $Cl(^2P_J)$ REACTIONS WITH THE CHLOROETHANES CH_3CH_2Cl, CH_3CHCl_2, CH_2ClCH_2Cl, and $CH_2ClCHCl_2$

P. H. Wine* and D. H. Semmes

Molecular Sciences Group
Engineering Experiment Station
Georgia Institute of Technology
Atlanta, GA 30332

*Author to whom correspondence should be addressed

ABSTRACT

The kinetics of the reactions $Cl(^2P_J) + RHCl \rightarrow RCl + HCl$ were investigated over the temperature range 257-426 K for RHCl = CH_3CH_2Cl(k_2), CH_3CHCl_2(k_3), CH_2ClCH_2Cl(k_4), and $CH_2ClCHCl_2$(k_5). $Cl(^2P_J)$ was produced by 355 nm pulsed laser photolysis of Cl_2 and monitored by time resolved resonance fluorescence spectroscopy. The data are adequately described by the following Arrhenius expressions (units are $cm^3 molecule^{-1} s^{-1}$, errors are 2$\sigma$ and refer to precision only): $k_2 = (2.34 \pm 0.42) \times 10^{-11} \exp[-(310 \pm 56)/T]$, $k_3 = (8.19 \pm 1.84) \times 10^{-12} \exp[-(554 \pm 71)/T]$, $k_4 = (2.21 \pm 0.51) \times 10^{-11} \exp[-(793 \pm 73)/T]$, and $k_5 = (4.88 \pm 1.41) \times 10^{-12} \exp[-(786 \pm 88)/T]$. Under some experimental conditions evidence for $Cl(^2P_J)$ regeneration via a secondary reaction was observed. At 258 $\pm$ 1 K, deviations of $Cl(^2P_J)$ temporal profiles from first order behavior were attributable to the reactions $RCl + Cl_2 \xrightarrow{k_j} RCl_2 + Cl(^2P_J)$. By modelling the observed $Cl(^2P_J)$ temporal profiles, the rate constants k_j were found to lie in the range 5-12 $\times 10^{-14} cm^3$ $molecule^{-1} s^{-1}$ for all RCl investigated. The reactivity trends observed in reactions of $Cl(^2P_J)$ with $C_2H_xCl_{6-x}$, x=3-6, are discussed.

Kinetics of $Cl(^2P_J)$ Reactions With the Chloroethanes CH_3CH_2Cl, CH_3CHCl_2, CH_2ClCH_2Cl, and $CH_2ClCHCl_2$

Introduction

Reactions involving abstraction of a hydrogen atom by ground state atomic chlorine, $Cl(^2P_J)$, have been studied extensively by kineticists for many years. Early work, which employed end product analysis techniques to determine relative rate coefficients for reactions of $Cl(^2P_J)$ with hydrogen, alkanes, and chlorinated alkanes, was motivated by the desire to test the ability of various theories to predict the rate coefficients for a series of related reactions.[1,2] In recent years, the controversy concerning the extent of chlorine catalyzed destruction of stratospheric ozone[3] has led to renewed interest in reactions which convert $Cl(^2P_J)$ into the relatively stable reservoir species HCl; this has motivated the application of modern "direct" kinetic techniques in numerous investigations of $Cl(^2P_J)$ reactions with hydrogen-containing atmospheric constituents such as H_2, hydrocarbons, HO_2, and H_2CO.[4] A number of $Cl(^2P_J)$ + RH reactions have also been investigated as initiation reactions in model systems for studying chain reaction kinetics.[5]

Because chloroalkane concentrations in the stratosphere are relatively low, their reactions with $Cl(^2P_J)$ have received relatively little attention. Two studies of $Cl(^2P_J)$ reactions with chloromethanes have been reported,[6,7] while the only kinetic investigation of a $Cl(^2P_J)$ + chloroethane reaction reported to date is a recent study in our laboratory[8] of the reaction

$$Cl(^2P_J) + CH_3CCl_3 \longrightarrow CH_2CCl_3 + HCl. \qquad (1)$$

We found reaction (1) to be surprisingly slow -- at 298K $Cl(^2P_J)$ reacts with ethane at least 1300 times faster than with CH_3CCl_3. To better understand this unexpected result we decided to extend our measurements to include the following reactions:

$$Cl(^2P_J) + CH_3CH_2Cl \longrightarrow \text{products} \qquad (2)$$

$$Cl(^2P_J) + CH_3CHCl_2 \longrightarrow \text{products} \qquad (3)$$

$$Cl(^2P_J) + CH_2ClCH_2Cl \longrightarrow CH_2ClCHCl + HCl \qquad (4)$$

$$Cl(^2P_J) + CH_2ClCHCl_2 \longrightarrow \text{products}. \qquad (5)$$

The results of our investigations of reactions (2)-(5) are reported in this paper.

Experimental:

The experimental apparatus is described elsewhere.[8] $Cl(^2P_J)$ was produced by 355 nm pulsed laser photolysis of Cl_2 and detected by time resolved resonance fluorescence spectroscopy. A cw electrodeless discharge lamp (gas mixture: 0.1% Cl_2 in He) was used as the fluorescence excitation light source. The lamp output was filtered with a calcium fluoride window and an N_2O gas filter to prevent impurity emission of H, O, and N resonance radiation from entering the reactor. Signals were obtained using photon counting techniques in conjunction with multichannel scaling. All experiments were carried out under "slow flow" conditions. The linear flow rate through the pyrex reactor was 3 cm s^{-1} and the

laser repetition rate was 1 Hz. Under these conditions, a fresh reaction mixture was available for each laser shot. Dilute mixtures of the chloroethane reactant (RHCl) in argon were prepared in 12 liter bulbs. RHCl, Cl_2, Ar and, in some cases, O_2 were premixed before entering the reactor; the concentration of each component in the reaction mixture was determined from measurement of the appropriate mass flow rates and the total pressure. The fraction of RHCl in the RHCl/Ar mixtures was checked frequently by UV photometry at 185.0 nm (mercury resonance line). The required absorption cross sections were measured during the course of the investigation. They are (in units of cm^2): CH_3CH_2Cl: 1.34×10^{-19}, CH_3CHCl_2: 1.31×10^{-18}, CH_2ClCH_2Cl: 5.92×10^{-19}, and $CH_2ClCHCl_2$: 1.58×10^{-18}. The CH_3CH_2Cl cross section agrees well with a previously published value.[9]

The gases used in this study had the following stated purities: Ar > 99.995%, O_2 > 99.99%, Cl_2 > 99.9%, He > 99.999%, and CH_3CH_2Cl > 99.7%. CH_3CH_2Cl was degased repeatedly at 77K before use while all other gases were used as supplied. The CH_2ClCH_2Cl sample was Fisher reagent grade (no stabilizers added) and had an overall purity of ~99%. Special analyzed samples of unstabilized CH_3CHCl_2 and $CHCl_2CH_2Cl$ were obtained from Dow Chemical. The CH_3CHCl_2 sample had an overall purity of 99.76 mole %; major impurities were CH_3CH_2Cl (0.15 mole %), $CHCl{=}CHCl$ (0.07 mole %), and CH_3CCl_3 (0.015 mole %). The $CH_2ClCHCl_2$ sample had an overall purity of 99.20 mole %; major impurities were CH_2ClCCl_3 (0.48 mole %) and CH_2ClCH_2Cl (0.32 mole %). All liquid samples were purified by vacuum distillation with only the middle fraction used in experiments.

Results

All experiments were carried out under pseudo-first order conditions with RHCl in large excess over $Cl(^2P_J)$. Argon was used as the buffer gas at a pressure of 100 Torr, thus insuring that a thermal distribution of $Cl(^2P_J)$ spin-orbit states was maintained throughout the course of the reaction.[10] Typical atomic and molecular chlorine concentrations were $[Cl(^2P_J)]_o = 2 \times 10^{11}$ per cm^3 and $[Cl_2] = 6 \times 10^{13}$ per cm^3, although both concentrations were varied over a wide range as checks on the system chemistry.

To study the kinetics of reactions (2)-(5), it is desirable to establish experimental conditions where the $Cl(^2P_J)$ temporal profile is governed entirely by the following processes:

$$Cl_2 \xrightarrow{h\nu} 2\,Cl(^2P_J) \qquad (6)$$

$$Cl(^2P_J) + RHCl \xrightarrow{k_i} RCl + HCl,\ i = 2\text{-}5 \qquad (i)$$

$$Cl(^2P_J) \longrightarrow \text{loss by diffusion from detector field of view and reaction with background impurities.} \qquad (7)$$

Then, since $[RHCl] \gg [Cl(^2P_J)]$, simple first order kinetics are obeyed:

$$\ln\left\{[Cl(^2P_J)]_o/[Cl(^2P_J)]_t\right\} = (k_i[RHCl] + k_7)t = k't. \qquad (8)$$

The bimolecular rate constant, k_i is determined from the slope of a k' vs [RHCl] plot. Observation of $Cl(^2P_J)$ temporal profiles which are exponential (i.e. obey equation 8), a linear dependence of k' on [RHCl], and invariance of k' to variations in laser photon fluence and $[Cl_2]$ strongly suggests that reactions (i), (6), and (7) are the only processes which affect the $Cl(^2P_J)$ time history and, therefore, validates the measurement of k_i. The presence of reactive impurities in the RHCl samples would, of course, not be elucidated by the above set of observations (as long as $[\text{impurity}] >> [Cl(^2P_J)]$).

Over the entire range of experimental conditions investigated, factor of five variations in laser photon fluence had no effect on the observed $Cl(^2P_J)$ temporal profiles. This observation proves that biradical processes, such as reaction of $Cl(^2P_J)$ with a product of reactions (i) or with a photolytically produced radical, were unimportant. At T = 298K, all observed $Cl(^2P_J)$ temporal profiles were exponential with k' independent of both laser power and $[Cl_2]$. However, at both the lowest and highest temperatures investigated, non-exponential decays were observed. In all cases, the initial $Cl(^2P_J)$ decay rate was faster than the decay rate at later times. Since the forementioned variation in laser power demonstrated that the initial fast decay rate was not due to a radical-radical reaction, it must be that regeneration of $Cl(^2P_J)$ at long times via secondary reactions was the cause of the observed non-exponential temporal profiles. At $T \lesssim 298K$, non-exponential behavior could be eliminated either by reducing $[Cl_2]$ or by adding O_2 to the reaction mixture to scavenge the intermediate free radicals RCl. Hence, it appears that at low temperatures, non-exponential behavior was due to the reactions

$$RCl + Cl_2 \longrightarrow RCl_2 + Cl(^2P_J). \qquad (j)$$

At high temperatures the observed temporal profiles were insensitive to variations in $[Cl_2]$. However, non-exponential decays were not observed if O_2 was added to the reaction mixture. When sufficient O_2 was present (usually $\sim$ 0.5 Torr), exponential decays were observed and $k_i(T)$ was found to be independent of laser power, $[Cl_2]$, and further increases in $[O_2]$. At temperatures in the 400K range, and in the absence of O_2, drastic changes in kinetic behavior were observed for small ($\sim$10K) temperature increases, suggesting that the secondary reaction(s) of importance have large activation energies. Two possible secondary reactions which would result in $Cl(^2P_J)$ temporal profiles which are independent of variations in $[Cl_2]$ and laser photon fluence are

$$RCl \longrightarrow R + Cl(^2P_J) \qquad (k)$$

and

$$RCl + RHCl \longrightarrow ClRRH + Cl(^2P_J). \qquad (\ell)$$

Attempts to quantitatively model the secondary chemistry are described later in the paper. For determining $k_i(T)$, the important conclusion is that at all temperatures and for all RHCl it was possible to establish experimental conditions where $Cl(^2P_J)$ temporal profiles were exponential with a characteristic lifetime which was independent of $[Cl_2]$, $[O_2]$, and laser photon fluence but linearly dependent on [RHCl].

Nearly 300 experiments (experiment $\equiv$ determination of one pseudo-first order rate constant) were carried out. The attainable signal-to-noise ratio (S/N) was limited by absorption of resonance lamp radiation by RHCl and O_2; as a result S/N decreased dramatically as [RHCl] and $[O_2]$ increased. Typical high S/N data is

shown in Figure 1 while typical data obtained under conditions where S/N was low is included in Figure 5. Typical plots of k' vs [RHCl] are shown in Figure 2. Linear dependences of k' on [RHCl] were observed in all cases where decays were exponential. The experimental results are summarized in Table I. [Results of some preliminary experiments, which qualitatively examined the dependence of $Cl(^2P_J)$ temporal profiles on $[Cl_2]$ and laser photon fluence, are not included in Table I]. Those experiments where secondary chemistry complications were encountered are identified with asterisks; none of the data so identified were used to determine $k_i(T)$. Errors quoted for individual k_i determinations are 2σ and refer only to the precision of linear least squares fits of the k' vs [RHCl] data. Where two or more k_i values were averaged to obtain a rate constant, the overall precision is conservatively chosen to bracket all individual k_i's and their 2σ uncertainties. In those cases where only a single $k_i(T)$ was determined, the precision is set at $\pm$ 10%, which is a little larger than the typical uncertainty observed when several determinations were averaged. The absolute accuracy of the results is limited by precision and uncertainties in the determination of the reactant concentration. We estimate the absolute accuracy of each reported $k_i(T)$ to be $\pm$ 15%.

The data for reactions (2)-(5) are adequately described in Arrhenius form (i.e., a linear ln k vs T^{-1} dependence). Unweighted linear least squares analyses give the following Arrhenius expressions (units are cm^3 $molecule^{-1}s^{-1}$):

$$k_2 = (2.34 \pm 0.42) \times 10^{-11} \exp[-(310 \pm 56)/T]$$

$$k_3 = (8.19 \pm 1.84) \times 10^{-12} \exp[-(544 \pm 71)/T]$$

$$k_4 = (2.21 \pm 0.51) \times 10^{-11} \exp[-(793 \pm 73)/T]$$

$$k_5 = (4.88 \pm 1.41) \times 10^{-12} \exp[-(786 \pm 88)/T].$$

The errors in the above expressions are 2σ and represent precision only ($\sigma_A = A\sigma_{lnA}$). Experimental rate constants and best fit Arrhenius lines are plotted in Figure 3.

Secondary Chemistry

Based on the observations discussed above, we have attempted to model secondary chemistry using the following reaction mechanism:

$$Cl(^2P_J) + RHCl \longrightarrow HCl + RCl \qquad (i)$$

$$RCl + Cl_2 \xrightarrow{k_j} RCl_2 + Cl(^2P_J) \qquad (j)$$

$$RCl \xrightarrow{k_k} R + Cl(^2P_J) \qquad (k)$$

$$RCl + RHCl \xrightarrow{k_\ell} HRRCl + Cl(^2P_J) \qquad (\ell)$$

$$Cl(^2P_J) \xrightarrow{k_7} \text{loss by processes other than (i)} \qquad (7)$$

$RCl \xrightarrow{k_m}$ loss by processes which do not result in $Cl(^2P_J)$ production. (m)

The rate equations for the above reaction scheme can be solved analytically to yield the $Cl(^2P_J)$ temporal profile:

$$\frac{[Cl(^2P_J)]_t}{[Cl(^2P_J)]_o} = \frac{(K + \lambda_1)\, e^{\lambda_1 t} - (K + \lambda_2)\, e^{\lambda_2 t}}{\lambda_1 - \lambda_2} \qquad (9)$$

where $K = k_j[Cl_2] + k_k + k_\ell[RHCl] + k_m$

$\lambda_1 = 0.5\,\{(\alpha^2 - 4\beta)^{1/2} - \alpha\}$

$\lambda_2 = -0.5\,\{(\alpha^2 - 4\beta)^{1/2} + \alpha\}$

$\alpha = k_i[RHCl] + K + k_7$

$\beta = k_k k_\ell + k_j k_\ell [Cl_2] + k_i k_7 [RHCl] + k_\ell k_7.$

According to equation (9), if any (or all) of the secondary reactions (j), (k), or (ℓ) are important, a double exponential decay is observed with one component, i.e. λ_1 or λ_2, faster than the "primary" decay rate $k_i[RHCl] + k_7$.

Kinetic data for reactions (k) have been critically reviewed by Benson and O'Neal.[11] Based on their recommendations, rate constants for reactions (k) are calculated to be $\sim 10^{-5}$ s^{-1} at 258 K and about 100 s^{-1} at 400 K. Reactions (ℓ) are approximately thermoneutral and are expected to have substantial activation energies; hence, it seems safe to assume that these reactions are also negligibly slow at 258 K. It was not surprising, therefore, that the non-exponential decays observed at relatively high $[Cl_2]$ became well behaved (i.e. exponential) at low $[Cl_2]$. Except for a few trial calculations, which are discussed in more detail below, the model calculations for the 258 $\pm$ 1 K data assumed $k_k = k_\ell = 0$. Directly measured values for k_7, and k_i values obtained at low $[Cl_2]$ were used in the calculations. A trial and error procedure was employed to obtain the best pair of rate constants k_j and k_m to fit each temporal profile. A typical fit is shown in Figure 4, while a summary of all results is given in Table II. The data are fit very well by equation (9), giving k_j values of (5-12) x 10^{-14} cm^3 $molecule^{-1}$ s^{-1} for all RCl reactants. We estimate the accuracy of the k_j's determined from these model calculations to be $\pm$ 50% -- provided, of course, that the assumed mechanism includes all reactions of importance in producing and destroying $Cl(^2P_J)$.

If we relax the restriction that $k_k = k_\ell = 0$ at 258 K, then it is possible to reproduce the exponential decays observed at low $[Cl_2]$ by assuming values for k_i greater than or equal to those obtained under the assumption that $k_k = k_\ell = 0$ in conjunction with very fast rates for $(k_k + k_\ell[RHCl])$ and k_m. However, when such a choice of rate coefficients is employed, it is impossible to reproduce the non-exponential decays observed at higher $[Cl_2]$ because the slower components in the observed decays cannot accommodate the required fast k_m. Hence the observation of non-exponential decays at high $[Cl_2]$ and exponential decays at low $[Cl_2]$ leads to a fit for k_j and k_m which is unique within the confines of the proposed mechanism.

Even though reactions (j) certainly become faster with increasing temperature, no evidence for non-exponential $Cl(^2P_J)$ temporal profiles was observed at T = 298K. Due to an unidentified background reaction, $Cl(^2P_J)$ removal in the absence of RHCl, i.e., reaction (7), was found to be much faster at $T \geq 298K$ than at lower temperatures ($k_7 \sim 20\ s^{-1}$ at 258K and $\sim 75\ s^{-1}$ at 298K). Equation (9) predicts that for $k_j = 2 \times 10^{-13}$ cm^3 molecule^{-1}s^{-1} and $k_7 = 75\ s^{-1}$, deviations from exponential decays would be unobservable under the experimental conditions employed. Hence, the more rapid background $Cl(^2P_J)$ removal rate at higher temperatures made it unfeasible to determine activation energies for reactions (j). It is worth noting that in the presence of sufficiently large levels of Cl_2, evidence for reactions (j) should have been observable even with the faster value for k_7. However, an experimental problem, interference due to vacuum UV Cl_2 fluorescence excited by the chlorine resonance lamp, prevented experiments from being carried out under the required conditions.

Because non-exponential $Cl(^2P_J)$ temporal profiles were not observed at 298 K, the possibility that the observed $Cl(^2P_J)$ kinetics were influenced not only by reactions (1) and (7), but also by reactions(k), (ℓ), and (m) cannot be completely ruled out. However, the fact that addition of $\sim 2 \times 10^{16}$ O_2 per cm^3 to the reaction mixture had no effect on the observed kinetics argues strongly against this possibility. If we assume that addition of O_2 to RCl proceeds with a reasonable bimolecular rate coefficient of 5×10^{-13} cm^3 molecule^{-1} s^{-1} at 100 Torr Ar, then addition of 2×10^{16} O_2 per cm^3 to the reaction mixture would increase k_m by $10^4 s^{-1}$. The fact that the $Cl(^2P_J)$ kinetics were unaffected by addition of O_2 means, therefore, that either reactions (k), (ℓ), and (m) are of negligible importance or that, in the absence of O_2, $k_m >> 10^4\ s^{-1}$. The latter possibility seems virtually impossible in light of the fact that the data at 258 K suggest $k_m \sim 30\ s^{-1}$ at that temperature.

At temperatures above 400K, very complicated kinetic behavior was observed. $Cl(^2P_J)$ temporal profiles were non-exponential but independent of laser photon fluence and $[Cl_2]$. However, non-exponential decays were eliminated when RCl was scavenged by O_2. The occurrence of reactions (k) and/or (ℓ) is consistent with these observations. The fact that the observed temporal profiles did not become "more exponential" with increasing [RHCl] suggests that reactions (ℓ) were more important than reactions (k). However, as noted above, if any of the reactions (j), (k), or (ℓ) were regenerating $Cl(^2P_J)$, then double exponential decays would be observed with one component (λ_1 or λ_2) faster then $k_i[RHCl] + k_7$. Some typical high temperature data is shown in Figure 5. We find that it is not possible to fit traces such as (e) and (f) in Figure 5 using equation (9) in conjunction with measured values for k_7 and $k_i[RHCl]$. For any choices of k_j, k_k, k_ℓ, and k_m we find that the observed decay rate near t = 0 is sufficiently slow that the temporal profile in this time regime can be represented by equation (9) only if it is the slower component of the dual exponential decay which is observed, i.e. the fast component is rapid enough to be unobservable with the time resolution employed. Since the $Cl(^2P_J)$ decay rate becomes even slower at longer time, we are led to conclude that the reaction scheme used to model the system is incapable of explaining the kinetic observations at T> 400 K. Time resolved detection of additional reactive intermediates will be required to unravel the complex chemistry in this temperature regime.

Discussion

Arrhenius parameters and 298K rate coefficients for reactions (1)-(5) and the additional reaction

$$Cl(^2P_J) + CH_3CH_3 \longrightarrow \dot{C}H_2CH_3 + HCl \qquad (10)$$

are tabulated in Table III. The parameters for reaction (10) are those recommended by the NASA panel for chemical kinetic and photochemical data evaluation.[4] Data from other laboratories with which we can compare our results are extremely sparse. There have been no other absolute measurements of any of the rate coefficients k_1-k_5. A competitive kinetics measurement of the ratio k_2/k_{10} has been reported by Pritchard, et al.[12] By measuring the relative consumption of CH_3CH_3 and CH_3CH_2Cl in the presence of $Cl(^2P_J)$ these workers obtained the result $k_2/k_{10} = 0.38 \exp[-(250 \pm 50)/T]$. Using our results for $k_2(T)$ and the $k_{10}(T)$ taken from reference 4, we obtain $k_2/k_{10} = (0.304 \pm .042) \exp[-(220 \pm 140)/T]$. The agreement with the competitive kinetics results is excellent.

Our results demonstrate that substitution of Cl for H in ethane and chloroethanes dramatically reduces the "abstractability" of remaining H atoms. Both A-factors and activation energies are affected by Cl substitution, but the increase in activation energy with increasing Cl substitution is the dominant factor controlling the observed decrease in reactivity. The activation energy for the reaction of $Cl(^2P_J)$ with CH_3CCl_3 is found to be much larger than that for reaction with $CH_2ClCHCl_2$ even though both RHCl reactants contain the same number of H atoms and Cl atoms. A similar result is obtained for OH reactions with CH_3CCl_3 and $CH_2ClCHCl_2$.[13] Although C-H bond dissociation energies (BDE) do not seem to be available for any of the chloroethanes except $CHCl_2CCl_3$ and CH_2ClCCl_3,[14] it is tempting to speculate that substitution of Cl on one carbon atom (atom "a") substantially increases the strength of the C-H bonds on the adjacent carbon atom (atom "b"). Support for such speculation comes from the fact that CH_3CF_3, the fluorosubstituted analogue of CH_3CCl_3, is known to have

extremely strong C-H bonds (BDE = 106.7 kcal/mole[14]). On the other hand, thermodynamic data is available[15] which demonstrates that substitution of Cl for H in methane and chloromethanes decreases the dissociation energy of remaining C-H bonds. Kinetic data for H-abstraction from CH_xCl_{4-x} by $Cl(^2P_J)$ and $OH(X^2\Pi)$ are consistent with the idea that the rate of abstraction depends on the BDE, i.e., the fastest reactions are with $CHCl_3$ which has the weakest C-H bond and the slowest reactions are with CH_4 which has the strongest C-H bonds. If the reactivity trends observed in the chloromethane series are applicable to the chloroethanes as well, then substitution of Cl for H on carbon "a" not only strengthens C-H bonds on carbon "b", but also weakens remaining C-H bonds on carbon "a". Some end product analysis data is available which supports the contention that Cl substitution at carbon "a" increases the probability that H-abstraction will be from carbon "a"; for example, photolysis of Cl_2 in the presence of CHD_2CD_2Cl gives exclusively CHD_2CDCl_2 as a photoproduct[16]. The lower activation energy and lower A-factor we obtain for reaction of $Cl(^2P_J)$ with CH_3CHCl_2 compared to reaction with CH_2ClCH_2Cl is consistent with the hypothesis that H abstraction occurs primarily from the more substituted carbon atom, i.e., the lower activation energy suggests a weaker C-H bond at the reactive site while the lower A-factor is probably due, at least in part, to the presence of a single weakest C-H bond in CH_3CHCl_2 compared to four equivalent C-H bonds in CH_2ClCH_2Cl.

Rate constants for reactions of $C_2H_xCl_{5-x}$ radicals with Cl_2 have been obtained previously from studies of the photochlorination of ethylene and chloroethylenes. Most of this work was carried out by Dainton and co-workers and by Goldfinger and co-workers during the sixties. Pertinent references and recommended rate constants are given by Kerr.[17] Addition of $Cl(^2P_J)$ to

unsymmetric chloroethylenes is believed to occur at the least substituted carbon atom.[18] Hence, many of the radicals produced in the photochlorination of ethylenes are different from those which are probably produced by H abstraction from ethanes. Nevertheless, a comparison of results is instructive. Based on the photochlorination results, A-factors for all $C_2H_xCl_{5-x} + Cl_2$ reactions are within a factor of two of 6×10^{-13} cm^3 $molecule^{-1}s^{-1}$ while activation energies increase from zero to ~ 5 kcal $mole^{-1}$ with increasing Cl substitution. Repulsion of the incoming Cl_2 by chlorine atoms on the carbon atom bearing the unpaired electron is thought to be the primary factor affecting reactivity while delocalization of the unpaired electron due to chlorine atoms on the carbon adjacent to that bearing the unpaired electron is thought to play a significant but less important role.[18] The magnitude of the rate constants we obtain at 258K is consistent with an A factor of 6×10^{-13} cm^3 $molecule^{-1}s^{-1}$ and an activation energy of ~ 1 kcal $mole^{-1}$. The reactivity trend predicted by the photochlorination studies is not evident in our results, but the large uncertainties associated with both sets of measurements, indirect identification of the identity of the $C_2H_xCl_{5-x}$ reactants, and the fact that the photochlorination studies were done at T >298K while our results were obtained only at T = 258 $\pm$ 1 K makes quantitative comparisons difficult. Real time measurements featuring direct detection of $C_2H_xCl_{5-x}$ are needed to definitively elucidate the reactivity trends in $C_2H_xCl_{5-x} + Cl_2$ reactions.

Acknowledgements

We would like to thank Dr. A. R. Ravishankara for many helpful discussions during the course of this work. We would also like to thank D. Gerard and S. Collier of Dow Chemical for supplying us with analyzed samples of unstabilized CH_3CHCl_2 and $CH_2ClCHCl_2$. This work was supported in part by the National Science Foundation through grant No. ATM-80-19040 and in part by the National Aeronautics and Space Administration through subcontract No. 954814 from the Jet Propulsion Laboratory.

References

1. G. C. Fettis and J. H. Knox, Prog. React. Kinet. 2, 1 (1964), and references therein.

2. H. S. Johnston and P. Goldfinger, J. Chem. Phys. 37, 700 (1962).

3. F. S. Rowland and M. J. Molina, Rev. Geophys. Space Phys. 13, 1 (1975).

4. "Chemical Kinetic and Photochemical Data for use in Stratospheric Modelling," Evaluation No. 5, JPL Publication 82-57 (1982), and references therein.

5. D. J. Nesbitt and S. R. Leone, J. Chem. Phys. 72, 1722 (1980); J. Chem. Phys. 75, 4949 (1981); J. Phys. Chem. 86, 4962 (1982).

6. R. G. Manning and M. J. Kurylo, J. Phys. Chem. 81, 291 (1977).

7. M. A. A. Clyne and R. F. Walker, J. Chem. Soc. Far. Trans. I 69, 1547 (1973).

8. P. H. Wine, D. H. Semmes, and A. R. Ravishankara, Chem. Phys. Lett. 90, 128 (1982).

9. C. Hubrich and F. Stuhl, J. Photochem. 12, 93 (1980).

10. A. R. Ravishankara and P. H. Wine, J. Chem. Phys. 72, 25 (1980).

11. S. W. Benson and H. E. O'Neal, "Kinetic Data on Gas Phase Unimolecular Reactions", NSRDS-NBS 21, 1970.

12. H. O. Pritchard, J. B. Pyke, and A. F. Trotman-Dickenson, J. Amer. Chem. Soc. 77, 2629 (1955).

13. K. Jeong and F. Kaufman, Geophys. Res. Lett. 6, 757 (1979).

14. D. F. McMillen and D. M. Golden, Ann. Rev. Phys. Chem. 33, 493 (1982).

15. S. Furuyama, D. M. Golden, and S. W. Benson, J. Amer. Chem. Soc. 91, 7564 (1969).

16. D. C. McKean and B. W. Laurie, J. Mol. Struct. 27, 317 (1975).

17. Handbook of Bimolecular and Termolecular Gas Reactions, Volume I, J. A. Kerr, editor, CRC Press, Boca Raton, Fla., 1981, page 319.

18. P. B. Ayscough, F. S. Dainton, and B. E. Fleischfresser, Trans. Far. Soc. 62, 1838 (1966).

TABLE I: Kinetic Data for the Reactions of $Cl(^2P_J)$ with RHCl. Data affected by secondary chemistry and, therefore, not used to determine k_1 are indicated by asterisks.

RHCl	T(K)	$10^{-13}[Cl_2]$ (cm^{-3})	$10^{-16}[O_2]$ (cm^{-3})	Laser Fluence (mJ cm^{-2})	No. of Experiments	Range of k' (s^{-1})	$10^{13}(k_1 \pm 2\sigma)$ $cm^3 molecule^{-1} s^{-1}$	$\langle 10^{13} k_1(T) \rangle$ $cm^3 molecule^{-1} s^{-1}$
CH_3CH_2Cl	258	8.3	0	20	6	27-784	70.3 ± 3.9	70.3 ± 7.3
	275	7.2	0	20	5	40-766	76.1 ± 2.9	76.1 ± 7.6
	299	6.0	0	25	5	96-1050	79.2 ± 1.5	
		6.4	0	5	4	87-826	79.6 ± 4.9	
		5.9	1.3	20	5	98-1150	82.4 ± 3.3	80.4 ± 5.7
	352	4.9	0	25	5	80-707	83.8 ± 8.7*	
	355	5.4	1.3	20	5	78-1180	102 ± 3	102 ± 10
	416	4.7	0	20	6	76-842	82.1 ± 4.3*	
	419	5.2	0.88	20	4	86-1070	110 ± 1	109 ± 13
		5.2	1.8	20	4	79-995	107 ± 11	
CH_3CHCl_2	258	4.0	0	20	6	23-683	9.74 ± 0.55	9.74 ± 0.97
		11.3	0	20	3	20-480	10.6 ± 0.3*	
	298	6.0	0	20	5	94-841	13.8 ± 0.6	
		6.5	0	20	4	69-712	12.0 ± 0.6	
		6.5	0	4	4	55-666	13.5 ± 0.8	
		6.5	1.8	20	6	104-629	11.0 ± 0.5	
		6.6	2.1	20	6	78-652	12.6 ± 0.6	12.6 ± 2.1
		5.8	0	20	4	66-658	16.2 ± 0.7	
	349	5.8	2.2	20	5	102-624	16.0 ± 1.0	16.1 ± 1.1
		4.9	0	20	4	85-636	18.6 ± 0.5*	
	412	4.9	2.0	20	5	79-716	22.0 ± 0.6	22.0 ± 2.2

TABLE I (continued)

RHCl	T(K)	$10^{-13}[Cl_2]$ (cm^{-3})	$10^{-16}[O_2]$ (cm^{-3})	Laser Fluence (mJ cm^{-2})	No. of Experiments	Range of k' (s^{-1})	$10^{13}(k_i \pm 2\sigma)$ $cm^3 molecule^{-1} s^{-1}$	$\langle 10^{13} k_i(T) \rangle$ $cm^3 molecule^{-1} s^{-1}$
CH_2ClCH_2Cl	257	3.1	0	20	5	22-574	9.70 ± 0.44	9.70 ± 0.97
		10.9	0	20	3	19-452	9.69 ± 1.05*	
	278	5.8	0	20	5	26-607	12.9 ± 0.9	12.9 ± 1.3
	298	3.1	0	20	6	103-638	14.9 ± 1.1	
		10.8	0	20	4	107-602	15.5 ± 0.4	
		10.8	0	4	4	104-524	13.9 ± 0.6	
		6.5	0	20	4	84-592	14.0 ± 0.2	
		5.1	0	20	5	69-635	14.3 ± 0.2	
		6.0	2.3	20	5	76-539	15.0 ± 0.6	14.6 ± 1.3
	303	6.5	1.9	20	5	122-568	17.3 ± 1.1	17.3 ± 1.7
	326	5.9	0	20	5	75-704	20.6 ± 0.9	20.6 ± 2.1
	350	5.4	0	20	6	84-829	23.1 ± 0.4	23.1 ± 2.3
	353	5.4	2.4	20	5	108-628	23.2 ± 0.7	23.2 ± 2.3
	365	5.2	0	20	5	67-644	24.3 ± 0.8	24.3 ± 2.4
	377	5.0	0	20	5	74-675	22.6 ± 0.6*	
	389	5.1	0	20	5	76-643	20.1 ± 1.4*	
	401	2.4	0	20	3	77-361	15.2 ± 0.8*	
		9.6	0	20	3	62-412	18.8 ± 0.3*	
		9.6	0	4	3	75-378	16.4 ± 1.3*	
	404	5.4	1.4	20	5	125-500	28.7 ± 1.3	
		4.8	3.2	20	5	85-643	31.6 ± 1.4	
		4.8	6.0	20	2	82-458	30.6	30.3 ± 2.9
	413	4.3	0	20	5	a	a	
	426	4.2	0	20	3	82-245	5.3 ± 0.2*	

Table I (continued)

RHCl	T(K)	$10^{-13}[Cl_2]$ (cm^{-3})	$10^{-16}[O_2]$ (cm^{-3})	Laser Fluence (mJ cm^{-2})	No. of Experiments	Range of k' (s^{-1})	$10^{13}(k_i \pm 2\sigma)$ $cm^3 molecule^{-1} s^{-1}$	$\langle 10^{13} k_i(T) \rangle$ $cm^3 molecule^{-1} s^{-1}$
$CH_2ClCHCl_2$	258	3.7	0	20	5	32-347	2.38 ± 0.11	2.38 ± 0.24
		7.6	0	20	2	23-162	2.75 *	
		13.9	0	20	2	18-162	2.81 *	
	275	2.9	0	20	3	54-368	2.68 ± 0.04	
		6.6	0	20	5	38-464	2.82 ± 0.21	2.75 ± 0.28
	298	2.5	0	20	3	72-430	3.24 ± 0.17	
		6.1	0	20	4	61-476	3.44 ± 0.06	
		6.1	0	4	4	63-460	3.31 ± 0.14	
		6.2	1.7	20	5	88-484	3.26 ± 0.34	3.31 ± 0.39
	347	5.4	0	20	4	84-534	4.81 ± 0.28*	
		5.4	1.7	20	5	108-609	5.38 ± 0.22	5.38 ± 0.54
	411	2.3	0	20	3	75-375	4.09 ± 0.14*	
		4.9	0	20	3	93-399	4.20 ± 0.07*	
		5.1	2.1	20	3	99-505	7.06 ± 0.73	
		5.1	3.5	20	4	94-412	7.04 ± 0.80	7.05 ± 9.81

[a] decays were such that k' values could not be estimated, i.e., not exponential for even a single 1/e time.

TABLE II: Kinetic data for the reactions RCl + Cl_2 $\xrightarrow{k_j}$ RCl_2 + $Cl(^2P_J)$ at 258 ± 1 K. Uncertainties in rate constants are estimated to be ± 50%.

RHCl	Possible RCl	k_i[RHCl] (s^{-1})	k_7(s^{-1})	10^{-14}[Cl_2] cm^{-3}	Best fit k_m(s^{-1})	Best fit k_j (10^{-14} cm^3 $molecule^{-1}$ s^{-1})
CH_3CH_2Cl	$CH_3\dot{C}HCl$	162	27	0.828	30	5
	$\dot{C}H_2CH_2Cl$					
CH_3CHCl_2	$CH_3\dot{C}Cl_2$	134	20	1.13	25	9
	$CHCl_2\dot{C}H_2$	478	20	1.13	40	13
		141	23	0.398	40	13
CH_2ClCH_2Cl	$CH_2Cl\dot{C}HCl$	121	19	1.09	38	7
		424	19	1.08	38	7
		118	23	0.318	10	7
$CH_2ClCHCl_2$	$CH_2Cl\dot{C}Cl_2$	131	18	1.39	27	7
	$CHCl_2\dot{C}HCl$	142	23	0.764	25	9

TABLE III: Arrhenius parameters and k(298K) for reactions of $Cl(^2P_J)$ with ethane and mono-, di-, and tri-chloroethanes. Units for A and k(298K) are 10^{-12} cm^3 $molecule^{-1}$ s^{-1}. Units for E/R are degrees Kelvin.

Reactant	A	E/R	k(298K)	Reference
CH_3CH_3	77	90	57	4
CH_3CH_2Cl	23.4	310	8.3	This work
CH_3CHCl_2	8.19	554	1.3	This work
CH_2ClCH_2Cl	22.1	793	1.5	This work
$CH_2ClCHCl_2$	4.88	786	0.35	This work
CH_3CCl_3		>1200	< 0.037	8

TABLE II: Kinetic data for the reactions RCl + Cl_2 $\xrightarrow{k_j}$ RCl_2 + $Cl(^2P_J)$ at 258 ± 1 K. Uncertainties in rate constants are estimated to be ± 50%.

RHCl	Possible RCl	k_i[RHCl] (s^{-1})	k_7(s^{-1})	10^{-14}[Cl_2] cm^{-3}	Best fit k_m(s^{-1})	Best fit k_j (10^{-14} cm^3 $molecule^{-1}$ s^{-1})
CH_3CH_2Cl	$CH_3\dot{C}HCl$	162	27	0.828	30	5
	$\dot{C}H_2CH_2Cl$					
CH_3CHCl_2	$CH_3\dot{C}Cl_2$	134	20	1.13	25	9
	$CHCl_2\dot{C}H_2$	478	20	1.13	40	13
		141	23	0.398	40	13
CH_2ClCH_2Cl	$CH_2Cl\dot{C}HCl$	121	19	1.09	38	7
		424	19	1.08	38	7
		118	23	0.318	10	7
$CH_2ClCHCl_2$	$CH_2Cl\dot{C}Cl_2$	131	18	1.39	27	7
	$CHCl_2\dot{C}HCl$	142	23	0.764	25	9

TABLE III: Arrhenius parameters and k(298K) for reactions of $Cl(^2P_J)$ with ethane and mono-, di-, and tri-chloroethanes. Units for A and k(298K) are 10^{-12} cm^3 $molecule^{-1}$ s^{-1}. Units for E/R are degrees Kelvin.

Reactant	A	E/R	k(298K)	Reference
CH_3CH_3	77	90	57	4
CH_3CH_2Cl	23.4	310	8.3	This work
CH_3CHCl_2	8.19	554	1.3	This work
CH_2ClCH_2Cl	22.1	793	1.5	This work
$CH_2ClCHCl_2$	4.88	786	0.35	This work
CH_3CCl_3		>1200	< 0.037	8

Figure Captions

1. Typical data obtained under conditions where signal-to-noise per laser shot was high, i.e., low [RHCl] and $[O_2] = 0$. Reaction: $Cl(^2P_J) + CH_3CH_2Cl$. Experimental condtions: T = 258K; $[Cl_2] = 8.3 \times 10^{13}$ molecules per cm^3; laser energy fluence = 20 mJ per cm^2; $[CH_3CH_2Cl]$ in units of 10^{13} molecules per cm^3= (a) 0, (b) 1.61, (c) 4.28, (d) 9.22; number of laser shots averaged = (a) 8, (b) 64, (c) 128, (d) 256. Pseudo-first order $Cl(^2P_J)$ decay rates obtained from the data are (a) 27 s^{-1}, (b) 187 s^{-1}, (c) 410 s^{-1}, (d) 784 s^{-1}.

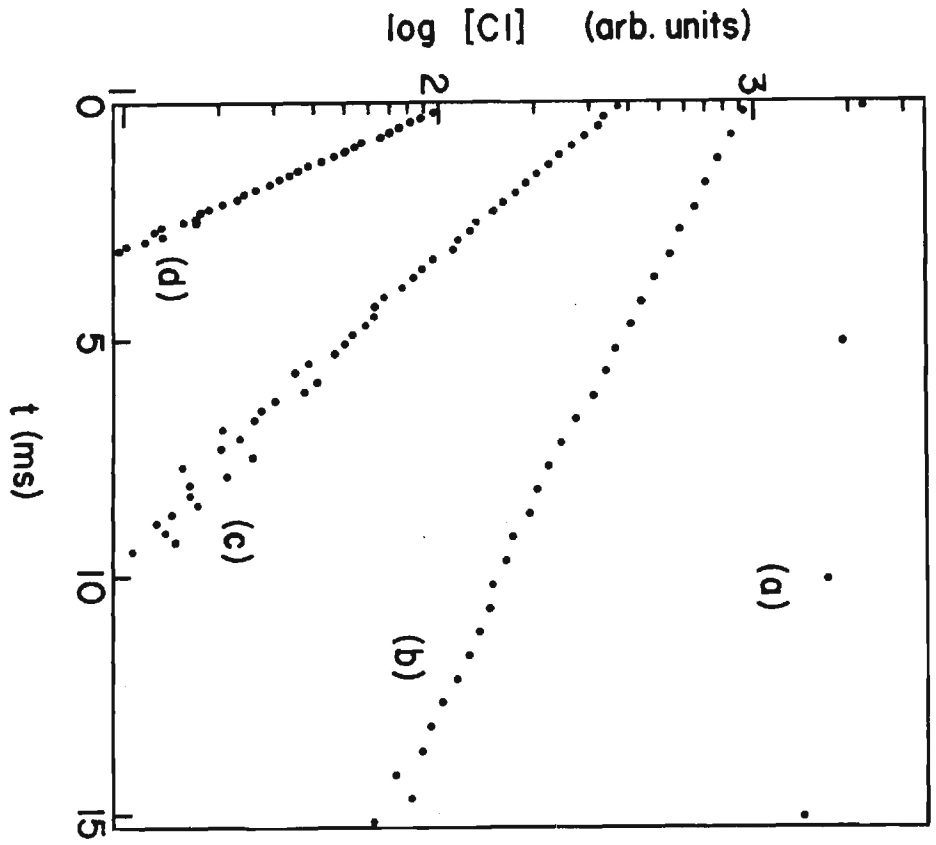
2. k' vs. $[CH_3CHCl_2]$ data obtained under conditions where secondary production of $Cl(^2P_J)$ was negligible. Solid lines are obtained from unweighted linear least squares analyses; the slopes of these lines give the bimolecular rate constants $k_3(T)$.

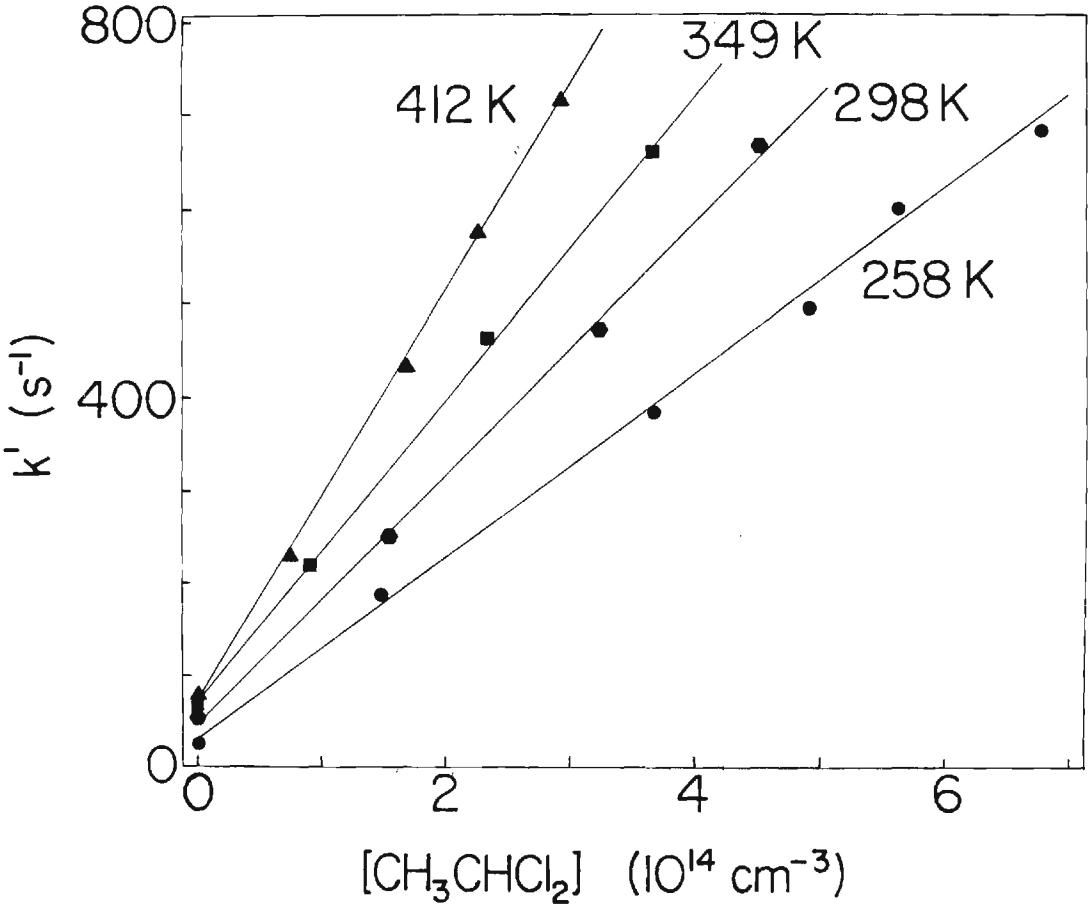
3. Arrhenius plots for reactions (2)-(5). Solid lines are obtained from unweighted linear least squares analyses.

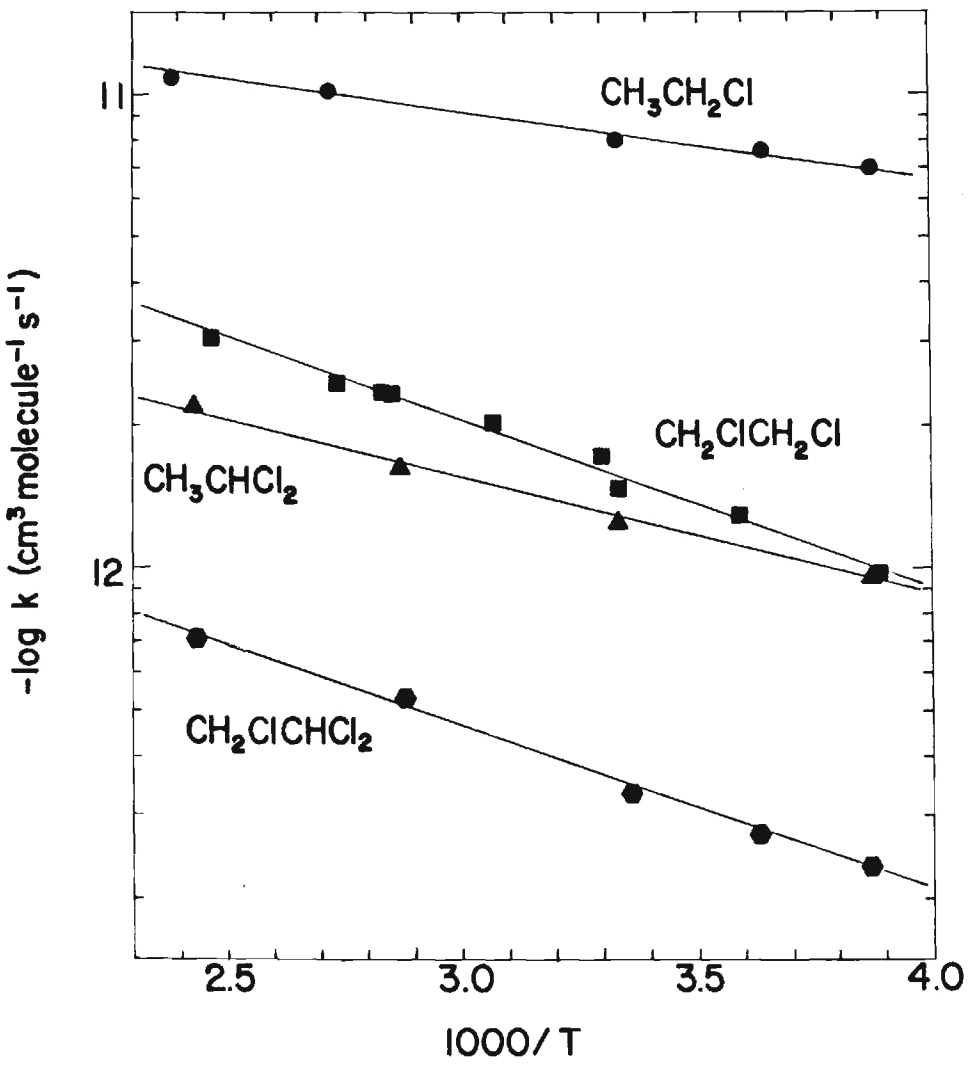
4. Typical $Cl(^2P_J)$ temporal profile at low T, high $[Cl_2]$. Reaction: $Cl(^2P_J) + CH_2ClCH_2Cl$. Experimental conditions: T = 257K, $[Cl_2] = 1.09 \times 10^{14}$ molecules per cm^3, laser energy fluence = 20 mJ per cm^2, 50 laser shots averaged. The solid line is obtained from a two parameter fit to equation (9) using $k_4[CH_2ClCH_2Cl] = 160\ s^{-1}$ and $k_7 = 19\ s^{-1}$ as determined in independent experiments and assuming $k_k = k_\ell = 0$. The best fit line is obtained for the choice of parameters $k_m = 38\ s^{-1}$ and $k_j = 7 \times 10^{-14}$ cm^3 $molecule^{-1}s^{-1}$.

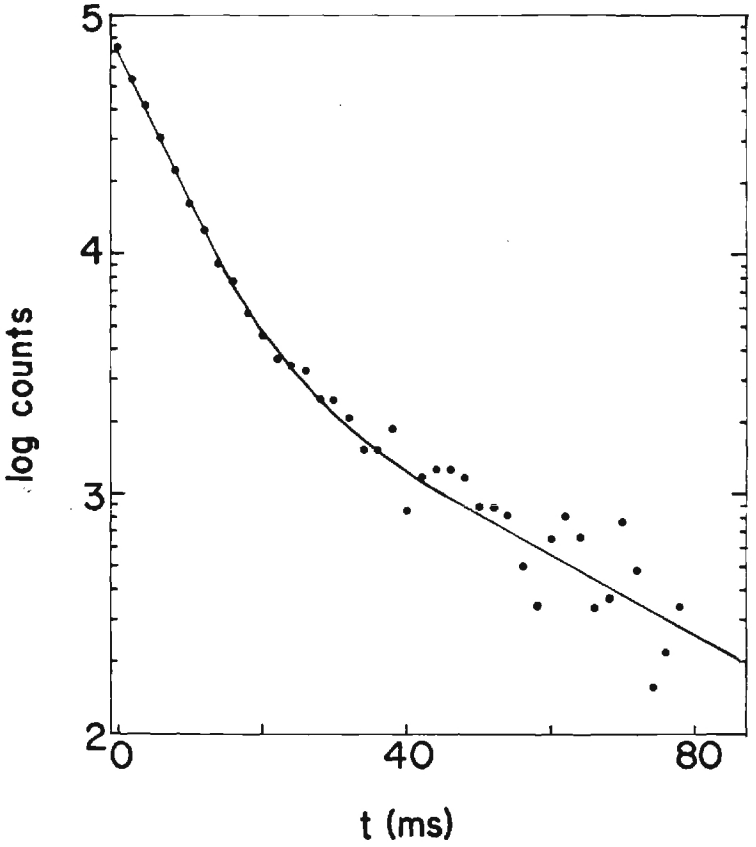
Figure Captions Continued

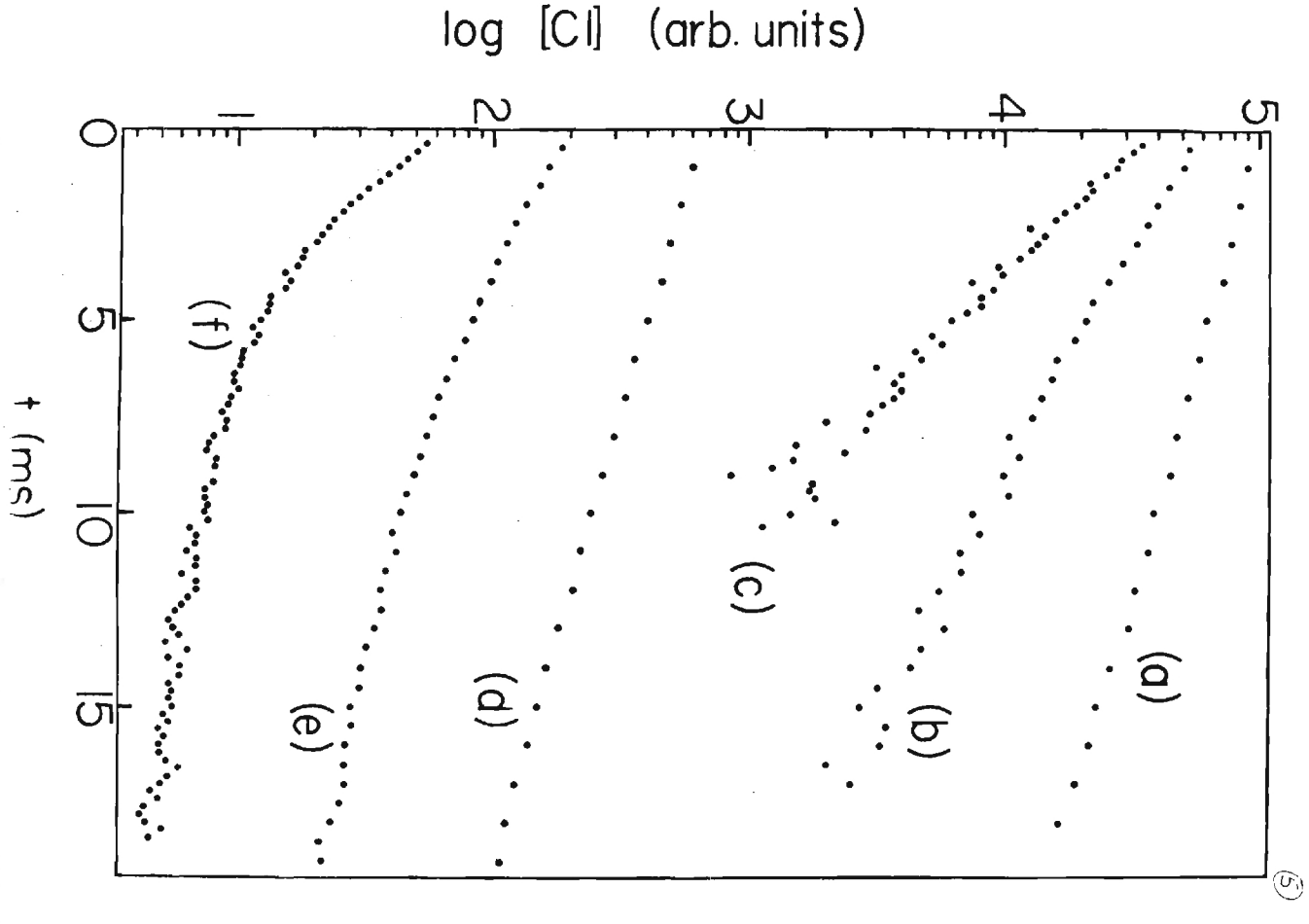
5. Typical $Cl(^2P_J)$ temporal profiles at T > 400K. Reaction: $Cl(^2P_J) + CH_2ClCHCl_2$. Experimental conditions: T = 411K; $[Cl_2] = 5.1 \times 10^{13}$ molecules per cm^3; laser energy fluence = 20 mJ per cm^2; $[O_2] = 3.5 \times 10^{16}$ molecules per cm^3 for (a)-(c), 0 for (d)-(f); $[CH_2ClCHCl_2]$ in units of 10^{14} molecules per cm^3 = (a) 0, (b) 1.60, (c) 3.52, (d) 0, (e) 2.30, (f) 7.28; number of laser shots averaged = (a) 64, (b) 128, (c) 300, (d) 25, (e) 128, (f) 256. In experiments (a)-(d), where $Cl(^2P_J)$ decays are exponential, the decay rates obtained from the data are (a) 94 s^{-1}, (b) 195 s^{-1}, (c) 355 s^{-1}, (d) 94 s^{-1}. Trace (c) is typical of the lowest quality data, i.e., poorest signal-to-noise, employed to determine the rate constants $k_i(T)$, i = 2-5.


log [Cl] (arb. units)
1
2
3
0
5
10
15
t (ms)
(d)
(c)
(b)
(a)


800
400
0
k' (s⁻¹)
412 K
349 K
298 K
258 K
0
2
4
6
[CH3CHCl2] (10¹⁴ cm⁻³)


-log k (cm³ molecule⁻¹ s⁻¹)
11
12
CH₃CH₂Cl
CH₂ClCH₂Cl
CH₃CHCl₂
CH₂ClCHCl₂
2.5
3.0
3.5
4.0
1000/T


log counts
5
4
3
2
0
40
80
t (ms)


log [Cl] (arb. units)
0
1
2
3
4
5
0
5
10
15
t (ms)
(a)
(b)
(c)
(d)
(e)
(f)